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AGRICULTURAL CHEMISTRY

A Reference Text

BY

DONALD E. H. FREAR, PH.D., Editor
Professor of Agricultural and Biological Chemistry,
The Pennsylvania State College

VOLUME TWO

PRACTICAL APPLICATIONS OF AGRICULTURAL CHEMISTRY

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LIST OF CONTRIBUTORS

C. A. Black, Iowa State College

A. D. Caesar, Caesar and Rivise, Attorneys

J. R. Clopton, University of Colorado

R. M. Conrad, University of Denver

D. E. H. Frear, The Pennsylvania State College

H. R. Guilbert, University of California

A. H. Johnson, National Dairy Research Laboratories, Inc.

Z. I. Kertesz, New York Agricultural Experiment Station, Geneva

R. C. Miller, The Pennsylvania State College

V. H. Morris, Federal Soft Wheat Laboratory

P. B. Pearson, U. S. Atomic Energy Commission

W. H. Pierre, Iowa State College

E. R. Purvis, Rutgers University

A. C. Richer, The Pennsylvania State College

C. W. Rivise, Caesar and Rivise, Attorneys

J. D. Romaine, American Potash Institute, Inc.

A. E. Schaefer, Alabama Polytechnic Institute

S. E. Smith, Cornell University

J. T. Sullivan, U. S. Regional Pasture Research Laboratory

S. F. Thornton, F. S. Royster Guano Company

H. W. Titus, Limestone Products Corporation of America

H. W. Von Loesecke, Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture

C. F. Winchester, Bureau of Animal Industry, U. S. Department of Agriculture

PREFACE

Agricultural chemistry, in its broadest sense, embraces every phase of chemistry as it is related to the growing and processing of economic plants and animals. It is obvious that in such a tremendously large field a complete discussion of all of the varied phases of the subject would fill many volumes. Such an undertaking would be extremely difficult, and it is hardly likely that an inclusive compendium of this nature will be prepared in the immediate future.

Several books on agricultural chemistry are, however, available. These present the subject in a condensed form and are intended primarily as teaching texts for elementary courses in agricultural colleges and universities. Although they serve this purpose well enough, they are decidedly unsatisfactory for the serious student of the subject. For a number of years there has been a need for a reference text on agricultural chemistry. Enrollment of graduate level students in institutions throughout the country has increased phenomenally within recent years, and courses in specialized phases of agricultural chemistry are being offered more frequently than ever before. There is also a rapidly increasing number of specialists engaged in agricultural work—county agents, Federal and state extension workers, and representatives of commercial firms—whose work involves the development, promotion, sale or application of such products as feeds, fertilizers, insecticides, fungicides and herbicides. These individuals frequently require specific information on the chemistry of the products and processes with which they are dealing. Finally, there is a large body of research investigators in the agricultural sciences who frequently seek information on subjects bordering on their own specialty. All of these individuals have need for a general reference text on agricultural chemistry, and many have expressed the desire for such a book.

These two volumes present a detailed discussion on each of the more important phases of agricultural chemistry. Since the field is so broad, no one man could be expected to prepare a competent discussion of the many highly specialized phases of the subject. The individual chapters have therefore been written by men who are recognized specialists. Although it is impossible to present an exhaustive dissertation on such a large subject, even in two volumes, the editor believes that each chapter, with the appended references, will enable the reader to secure a good general understanding of the subject under discussion.

The first volume of this work deals with the more fundamental phases of agricultural chemistry, including the chemistry of the basic compounds of biological importance, and of the physiological processes of plants and animals. The second volume is devoted to the practical applications of agricultural chemistry. Thus the first volume probably will be most useful to the teacher and research worker, while the second will be of more interest to the practicing agricultural specialist.

In order to eliminate as much elementary material as possible, it has been assumed that the reader has a good general knowledge of inorganic and organic chemistry. Nearly all technical university curricula include these subjects, and many excellent texts are available on the fundamentals of chemistry.

The editor is of the opinion that technical writers should be permitted to present their scientific work in their own words. Editorial changes in the manuscripts submitted for these two volumes have been kept to a minimum, and only a few chapters required extensive revision. Occasional minor changes were made in certain other chapters, but most of them appear substantially in the form in which they were originally written. The generally high quality of the manuscripts has made the editor's task an easy one, and it has been a pleasure to assemble these volumes.

To each of the chapter authors the editor extends his thanks for a job well done. Special credit should be given to the many indivduals who contributed suggestions and ideas for the book: mention should be made of the valuable assistance rendered by Drs. R. A. Dutcher, C. O. Jensen, H. O. Triebold, R. V. Boucher, and R. C. Miller, who read sections of the manuscript and offered helpful suggestions. The editor also expresses his appreciation to the many individuals who kindly gave permission to reproduce published figures, charts and data. These have been acknowledged in the appropriate places in the text.

It is hoped that the information contained in these two volumes will prove valuable to those who use them. The editor will welcome comments and suggestions from readers at any time.

DONALD E. H. FREAR

State College, Pa.
July, 1951.

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PART I

CHEMISTRY OF MAJOR AGRICULTURAL PRODUCTS

Chapter I

THE CHEMISTRY OF SEED AND CEREAL CROPS

V. H. Morris [*]

Formerly of the Soft Wheat Quality Laboratory, U. S. Department of Agriculture, Wooster, Ohio

As sources of food and feeding stuffs the two groups of seed-producing plants of foremost importance are the grasses, belonging to the botanical family *Gramineae*, and the legumes, of the family *Leguminosae*. The most important members of the grass family are the cereals, including, wheat, corn, barley, oats, rye, rice, and sorghum. The significance of cereals in world and national economy arises from the fact that they represent the most important source of carbohydrates in concentrated form for both man and beast. As sources of food energy, they far outweigh all other foodstuffs.

Another group of seeds of major importance are the so-called oil seeds. These are valuable from two standpoints: (1) the production of oil important for both edible and industrial purposes, and (2) the residue or cake remaining after removal of the oil which is valuable as animal feedstuffs. The more important of these oil seeds are cotton, flax, peanuts, and soybeans. The last two named are legumes.

The origin of the cereal and seed crops both as to geographical location and to ancestry has long been a matter of conjecture. Most of these crops were under cultivation at the dawn of recorded history, and thus their place of origin and wild ancestors are largely unknown. It is commonly considered, however, that the original home of all the important grains was in very hot climates. Now only rice and sorghum are considered hot climate grains, the others producing best in temperate zones. Of the cereal and seed crops produced in the United States only one—corn—was indigenous to the Americas, the others all postdating colonization.

WHEAT

Wheat is grown under a great variety of climatic conditions, but the most extensive wheat-growing areas have moderate temperatures and subhumid climates. Under conditions favoring its survival fall-sown or winter wheat produces the highest and most stable yields; approximately

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[*] Dr. Morris died in 1949, shortly after the manuscript for this chapter was completed. Drs. Lamb, Sayre and Yamazaki, former associates of the author, have been kind enough to read proof and give technical advice on the chapter.

Editor

three-quarters of the world's crop is of this type. In areas where winter temperatures are limiting factors, however, wheat is spring-sown. The world average annual production of wheat for the period 1935–39 was nearly 6 billion bushels, with the production in the United States and Canada accounting for about one-sixth of the total (Table 1).

The three botanical species grown commercially in the United States are *Triticum aestivum* (*T. vulgare*) (common wheat), *T. durum* (amber and red durum wheat), and *T. compactum* (white and red club wheat). The first-named accounts for nearly 95 per cent of the production. The five classes of wheat which are commercially important in the United States, and the percentages of the average annual production[5] (1937–44, inclusive) of 897,352,000 bushels represented by each are: hard red winter, 43.5 per cent; soft red winter, 22.3 per cent; hard red spring, 19.9 per cent; durum (amber and red), 4.1 per cent; and white wheats (including club), 10.1 per cent.

The hard red winter wheat region centers in the central portion of the Great Plains, the greatest acreages occurring in Kansas, Oklahoma, Nebraska, and Texas. The region is characterized by cold, dry winters, and annual precipitation varying from 15 to 30 or 35 inches. Some of the leading varieties are Pawnee, Comanche, Tenmarq, Triumph, Turkey, Wichita, and Westar.

Soft red winter wheat is grown chiefly in the eastern half of the United States, a region which is characterized by ample but not excessive rainfall and by moderately cold winters. The more important varieties are Thorne, Fultz, Fulcaster, Clarkan, Vigo, and Redhart.

Hard red spring wheat is grown chiefly in the northern portion of the Great Plains where the winters are generally too severe for winter wheat, an area including the two Dakotas and parts of Minnesota and Montana. The annual rainfall varies from about 15 to 25 inches. Important varieties are Thatcher, Mida, Rival, Ceres, Marquis, Rescue, and Cadet. Durum wheat is also grown in the spring wheat region. The leading durum varieties are Stewart, Carleton, and Mindum.

White wheat is grown principally in the far western states of Washington, Oregon, California, Idaho, and in New York and Michigan. The great variety of climate in the far western region is suggested by the multiplicity of types and classes, which include hard and soft, winter and spring, white and red. Leading varieties of western white wheat are Baart, Elgin, Rex, and Federation; eastern acreage is principally Yorkwin and Cornell 595.

The principal uses of wheat in the United States are for seed, feed, and food, the latter accounting for about two-thirds of the total. Except for the relatively minor products as breakfast cereals, macaroni, and spaghetti, the largest portion of the wheat consumed for food is

TABLE 1. GRAINS AND OIL SEEDS; PRODUCTION IN SPECIFIED AREAS, AVERAGES 1935–1939[*]

	Wheat 1000 bushels	Corn 1000 bushels	Barley 1000 bushels	Oats 1000 bushels	Rye 1000 bushels	Rice 1000 bushels	Cottonseed 1000 tons	Flaxseed 1000 bushels	Peanut 1000 pounds	Soybeans 1000 bushels
North America										
United States	758,623	2,315,539	238,616	1,045,329	44,917	49,852	5,554	10,991	1,229,204	56,167
Canada	312,399	7,010	88,882	338,071	9,191			1,508		207
Estimated Total [1]	1,086,000	2,423,200	331,000	1,384,000	54,108	64.100	5,735	12,700	1,279,000	
Europe										
Estimated Total [1]	1,626,000	735,000	719,000	1,745,000	898,000	53,100	75	9,500	82,700	
Asia										
India	370,660	83,368	103,619			1,904,819	2,591		6,591,424	
China	715,536	272,513	343,158	60,317		2.623,383	1,593		5,357,893	204,444
Estimated Total [1]	1,442,000	598,000	768,000			7,124,600	6.265 [3]	20,400 [2]	13,637,000	
Africa										
Estimated Total [1]	143,000	260,000	121,000			103,700	1,490	500	3,348,100	
South America										
Argentina	221,769	301,986	22.586	50,182	9,771	3,112		59,571	174,501	
Brazil	4,657	215,161				66,449			29,522	
Estimated Total [1]	281,000	566,000				89,400		64,200	257,000	
Oceania										
Australia	169,744	7,030	11,651	23,351	167	2,117			12,236	
Estimated Total [1]	176,873					2,700		24	13,000	
Estimated World Total [1]	5,914,000	4,721,000	2,338,000	4,362,000	1,728,000	7,447,000	14,895	136,900 [2]	18,616,800	456,600

[*] Compiled from Agricultural Statistics, 1946. U. S. Department of Agriculture.[5]

[1] Estimated totals include allowance for missing data for countries shown and for other producing countries not listed.

[2] Excludes China.

[3] Includes Soviet Union.

converted into flour and consumed as bread and pastry products. The process of milling wheat into flour has as its objective the separation of the white endosperm from the bran (and germ) with as little contamination by the latter as possible and the subsequent pulverization of the endosperm into flour. Preliminary processes consist of removal of weed seeds, dirt, and other foreign materials through a process of cleaning and scouring, followed by conditioning the grain for milling. Wheat is considered conditioned for milling when it has the proper moisture content and distribution to accomplish the following: (1) to produce maximum toughness of the bran to minimize its breaking up into particles of the fineness of flour, (2) to flatten the germ into large particles, and (3) to render the endosperm friable and thus capable of being fractured into particles as desired by the miller. In the modern process of milling the cleaned and conditioned wheat is subjected to a series of grinding operations, called "breaks" and "reductions," each followed by one or more sifting operations, combined in some instances with air aspiration. An excellent detailed description of modern milling technology is given by Geddes.[22]

The principal milling product is flour, which represents 70–75 per cent of the weight of the wheat. The by-products bran and shorts or middlings constitute the remaining 25–30 per cent and are used as livestock feed. The flour may be undivided, in which case it is known as "straight grade," or it may be divided into "patent," "clear," "low grade," and sometimes "red dog" flours. The patent flour, containing the portions of the total flour that are freest from bran particles and best in quality, may represent 30 to 95 per cent of the straight flour. "Clear" flour is the second-grade flour fraction and is sometimes divided into "first" and "second" clear. "Low grade," representing 1 to 5 per cent, is usually the poorest grade flour, but if an unusually long extraction is made, a still lower grade known as "red dog" is produced.

The importance of wheat as a food is due largely to the unique property of the endosperm proteins of forming gluten when wetted with water. When wheat flour is mixed with water, the proteins hydrate, forming gluten, a typically ductile, tenacious, elastic coherent mass. It is the gluten forming the network or skeleton which imparts to wheat flour doughs the property of gas retention and thus makes possible light leavened products. Crude gluten may be recovered from flour by kneading the dough in a stream of water which removes the starch and water-soluble components. Extensive studies have shown, however, that the percentage of crude protein serves to indicate the gluten content and, since the former can be determined with greater precision, it is generally to be preferred from the standpoint of a quantitative determination. In considering the utility of flours, not only must the variations in quantity of gluten be considered but also marked differences in quality or physical properties of the gluten. These variations in quality cannot at the present time be traced to differences in composition of the proteins but are generally considered to be associated with colloidal characteristics.

The quantity and quality of the gluten determine, to a large degree, the use for which a wheat flour is most suitable. For the production of yeast leavened bread, flours classified as "strong" are most suitable. Strong flours, generally milled from hard wheats, are characterized by a relatively high percentage of protein, with coherent, tough, extensible, elastic gluten properties. Such flours are said to be of good quality if, in addition to baking into large well-rounded loaves with good crumb grain and texture, they also have the following characteristics: (1) they require relatively large quantities of water to make a dough of standard consistency, thus producing a high yield of bread per unit weight of flour, and (2) they handle well in the bakeshop and are not critical in mixing and fermentation requirements. For the production of most pastries (chemically leavened products), flours classified as "weak" are preferred. Weak flours are generally milled from wheats grown in the mild, humid areas of the eastern and Pacific Coast regions, which produce fine, soft flours relatively low in protein. The chief property associated with these flours is that the gluten is soft, tender, nonelastic, and easily torn. By reason of these gluten properties they are regarded as superior for the production of chemically leavened products such as cakes and cookies.

TABLE 2. KIND, QUANTITY AND VALUE OF PRODUCTS MADE FROM WHEAT IN THE UNITED STATES, 1939 *

Products	Production 1000 lb.	Value
Wheat and prepared flours, total	21,828,270	$458,356,323
White flour, for sale as such	18,794,672	388,443,625
White flour, blended, plain	78,987	1,657,410
White flour, phosphated	662,734	14,351,017
White flour, self-rising	1,057,312	24,895,496
Other prepared flours [biscuit, cake, doughnut, pancake, etc.]	140,717	6,705,072
Semolina	665,184	13,423,319
Graham and whole-wheat flour	428,662	8,880,384
Bran and middlings	8,999,846	91,896,004
Breakfast foods		
Ready to serve	299,539	37,665,239
To be cooked before serving	153,453	10,463,153

* Data from Manufacturers' Census.[6]

While flours may in general be divided into these two classes, strong and weak, flours of varying degrees of strength or weakness are utilized by the bakery trade. The great variety of baked products of any particular type, such as bread or cake, produced under varying conditions, in the home, in large or small shops, require varying degrees of strength or weakness within the two classes.

TABLE 3. PROXIMATE COMPOSITION OF CEREALS AND SEEDS *

	Protein %	Fat %	Fiber %	N-Free Extract %	Ash %
Barley, common [1]	11.8	2.0	5.7	68.0	2.9
Barley [2]	8.7	1.9	5.7	71.0	2.6
Buckwheat	11.9	2.4	10.3	63.8	2.0
Corn, dent	9.7	4.0	2.3	71.1	1.4
Corn, flint	9.8	4.3	1.9	71.0	1.5
Oats [1]	12.0	4.7	10.6	60.2	3.6
Oats [2]	9.0	5.4	11.0	62.1	3.7
Rice, brown	8.9	2.0	1.0	77.2	1.1
Rice, polished	7.4	0.4	0.4	79.1	0.5
Rye	12.3	1.7	2.3	71.7	2.0
Sorghum	9.8	3.3	2.3	71.6	1.8
Wheat	13.1	1.7	3.0	70.0	2.0
Cottonseed	23.0	23.0	16.9	26.3	3.5
Flaxseed	23.5	36.4	5.9	24.2	3.6
Peanuts, kernels	30.5	47.7	2.5	11.7	2.3
Soybeans	36.9	17.2	4.5	26.3	5.3

* Taken by special permission of the Morrison Publishing Company, Ithaca, New York, from the Appendix Tables of "Feeds and Feeding," 20th ed. by F. B. Morrison.[37]

[1] Not including Pacific Coast states.

[2] Pacific Coast States.

The relative production and value of the more important types of wheat flours, as well as breakfast foods and mill by-products are summarized in Table 2. Most of the "white flour, for sale as such" is hard wheat flour utilized for the production of bread and yeast leavened products, whereas the "phosphated," "self-rising" and other prepared flours are milled from soft wheats and used for the production of biscuits, cakes, doughnuts, and other chemically leavened products.

Durum wheat is for the most part utilized in the production of the so-called "alimentary pastes"—macaroni, spaghetti, noodles, etc. For these purposes it is milled into coarsely ground, highly purified middlings

TABLE 4. CHEMICAL COMPOSITION OF A COMMERCIAL MILLING MIX OF HARD RED SPRING WHEAT AND THE PRODUCTS THEREOF *

Product	Milling Yield or Proportion of Whole Kernel %	Chemical Constituents							
		Moisture at Time of Milling %	Basis 13.5 Per Cent Moisture						
			Protein [Nx5.7] %	Fat %	Ash %	Starch[1] %	Pentosans %	Sugar %	Undetermined %
Wheat[2] [whole grain]	100.0	15.6[c]	15.28	1.87	1.85	53.0	5.17	2.61	6.75
Products therefrom:									
Patent flour	65.3	13.8	14.25	0.91	0.42	66.7	1.58	1.25	1.39
First clear flour	5.2	12.5	15.19	1.43	0.65	63.1	2.03	1.37	2.81
Second clear flour	3.2	13.4	18.09	2.43	1.41	56.3	2.56	2.09	3.65
Red dog flour	1.3	12.0	18.54	3.79	2.71	41.4	4.48	4.60	10.96
Shorts	8.4	13.5	18.49	5.25	4.99	19.3	13.80	6.72	18.01
Bran	16.4	13.8	16.71	4.58	6.50	11.7	18.10	5.48	23.46
Germ	0.2	13.8	30.91	12.60	4.32	10.0	3.68	16.61	8.36

* Data from Northern Regional Research Laboratory.[8]

[1] Starch determination by A.O.A.C. diastase method.

[2] Tempered Wheat.

[c] Before tempering this wheat had a moisture content of 11.9%.

TABLE 5. APPROXIMATE PERCENTAGE OF AMINO ACIDS IN PLANT PROTEINS * [1]

Amino Acids	Cereals											Oil Seeds			
	Corn				Wheat					Oats	Rice	Cotton-seed Meal	Linseed Meal	Peanut Flour	Soybean Meal
	Grain	Germ	Gluten	Zein	Grain	Germ	Gliadin	Gluten	Flour						
Arginine	4.0	6.8	3.1	1.6+0.2	2.8±0.5	6.0	2.6±0.2	3.9	3.9	6.0	7.2	7.4	6.9	9.9	5.8
Histidine	2.4	2.7	1.7	0.9±0.2	1-2	2.5	1.6±0.2	2.2	2.2	2.0	1.5	2.6	1.9	2.1	2.3
Lysine	2.0	5.8	1.1	0.0	2.7	6.4	0.7	1.9	1.9	3.3	5.2	2.7	2.0	3.0	5.8
Tyrosine	6.1	4.9	6.2	5.0±1.2	3.8±1.0	3.8	2.8±0.4	3.8	3.8	4.5	5.6	3.2	5.1	4.4	4.1
Tryptophane	0.8	1.3	0.6	0.1	1.2	1.0	0.8±0.1	1.0	0.8	1.3	1.3	1.3	1.6	1.0	1.6
Phenylalanine	5.0	5.6	6.6	6.4±0.7	5.7	4.2		5.5	5.5	6.9	6.3	6.8	5.8	5.4	5.7
Cystine	1.1	1.2±0.3	1.2	0.8±0.1	1.3±0.3	0.6	2.1±0.2	1.7	1.9	1.8	1.4	2.0	1.9	1.6	0.6±1.4
Methionine		2.3	4	2.0	2.0	2	2.1	3	3	2.3	3.4	1.6	2.3	1.3	2.0
Serine															
Threonine	3.6	4.4	4.0	2.4	3.3	3.8	2.7	2.5	2.7	3.5	3.9	3.0	4.5	1.5	4.0
Leucine	21.5±2.4	6.7	24.7±3.7	23.7±2.1	5.8	7.4±2.3	6.1		9.1	8.0	9.0	5.0	7.5±2.8	5.5	6.6
Isoleucine	3.6±0.3	3.7±0.4	4.9±0.3	4.3±0.4	3.3	3.0±0.5			4.5	5.3	5.1	3.4	3.4±0.3	3.4	4.7
Valine	4.6±0.7	5.8±1.2	4.6±1.4	2.4±0.9	3.6	4.1±1.0			5.0	6.5	6.4	3.7	5.8±1.3	4.0	4.2
Glutamic acid			24.5±0.4	35.6			42	27							
Aspartic acid				3.4			1.3	10							
Glycine			4.3	0.0			0-1	9	7.2			5.3		5.6	
Alanine				9.9			2-3	5							
Proline				9-12			12	10							
Hydroxyproline				1											

* Taken by permission from "The Amino Acid Composition of Proteins in Foods" by R. J. Block and D. Bolling, published by Chas. C. Thomas, Springfield, Ill.[15]

[1] Calculated to 16.0 gm. of nitrogen.

TABLE 6. THE MINERAL ELEMENT COMPOSITION OF CEREAL GRAINS AND OIL SEEDS *

	Barley		Buckwheat		Corn		Oats		Rice	
	No. of Analyses	Average %	No. of Analyses	Average %	No. of Analyses	Average %	No. of Analyses	Average %	No. of Analyses	Average %
Potassium	133	0.55			44	0.40	99	0.48	15[1]	0.38
Calcium	252	0.064			127	0.015	170	0.10	10[1]	0.090
Magnesium	170	0.14			121	0.16	76	0.16	7[1]	0.16
Phosphorus	316	0.41	9	0.33	197	0.43	233	0.34	18[1]	0.36
Sulfur	165	0.17			22	0.14	52	0.19		
Arsenic [x10^{4}]	2	0.33			2	0.19				
Barium [x10^{3}]					1	0.9				
Boron [x10^{3}]	1	0.2								
Bromine [x10^{3}]		0.55				0.17		0.31		
Chlorine	29	0.17			16	0.024	38	0.13		
Cobalt [x10^{5}]				3.6		0.11		Tr.		0.06
Copper [x10^{2}]	12	0.16			6	0.08	29	0.11	3	0.04
Fluorine [x10^{2}]				0.253						0.094
Iodine [x10^{4}]	5	0.102			21	0.177	13	0.057	1	0.040
Iron [x10^{2}]	23	0.99	1	0.34	4	0.37	34	0.79	3	0.19
Manganese [x10^{2}]	12	0.19			13	0.13	16	0.51	4	0.12
Nickel [x10^{4}]				1.34		0.14		0.45		0.02
Selenium [x10^{2}]										
Sodium	33	0.07			18	0.048	36	0.09	7[1]	0.10
Titanium [x10^{3}]		0.09		0.3		0.14		0.13		Tr.
Zinc [x10^{2}]	1	0.21	1	0.12	1	0.20	1	0.22	3	0.13

* Compiled from Beeson.[13]

[1] Paddy or rough rice.

called semolina. Quality in macaroni is reflected in hard, brittle, translucent pieces with an intense, clear yellow color and which on boiling swell to at least twice their original size without losing shape or firmness or becoming pasty. The amber durums are, in general, superior to the red varieties in meeting these specifications. Although grown in the same region as hard red spring wheat, durum wheats are superior for macaroni products but inferior for bread baking. The durum wheats differ principally in being harder and more vitreous, with a higher concentration of carotenoid pigments, as well as some differences in properties of gluten and starch. For further details on the production, properties, and utilization of durum wheat and its products the reviews of Le Clerc[34] and Alsberg[2] may be consulted.

TABLE 6. THE MINERAL ELEMENT COMPOSITIONS OF CEREAL GRAINS AND OIL SEEDS—CONTINUED

Rye		Sorghum		Wheat		Cottonseed		Flax		Soybeans	
No. of Analyses	Average %	No. of Analyses	Average %	No. of Analyses	Average %	No. of Analyses	Average %	No. of Analyses	Average %	No. of Analyses	Average %
11	0.53			264	0.48	10	1.20	1	0.63	29	1.83
10	0.115		0.081	290	0.050	10	0.15	1	0.28	9	0.24
4	0.14			267	0.17	5	0.35	1	0.43	7	0.31
71	0.37		0.22	310	0.40	10	0.75	14	0.59	37	0.78
3	0.18			138	0.18	3	0.26	1	0.06	6	0.24
				2	0.23						
				1	0.8					1	0.8
										5	1.9
	0.19										
4	0.02			80	0.09					2	0.03
					0.12						
2	0.07			108	0.09	1	0.54			1	0.12
5	0.083			26	0.067						
1	0.57			131	0.68	1	1.5	2	1.01	13	0.80
7	1.00			109	0.49	1	0.13	3	0.61	11	0.28
					0.35						3.92
					0.26						
4	0.04			100	0.07	3	0.31			6	0.24
	0.08				0.09						
1	0.13	1	0.14	27	0.63	1	3.20	1	0.20	1	0.18

Industrial uses for wheat other than food include the production of starch and gluten, industrial alcohol and potable spirits, malt, paste, and core-binder flour. Up to 1941 not more than a million bushels were used annually for all these industrial uses, but during World War II there was a marked increase in industrial utilization, principally as a source of alcohol in the production of synthetic rubber.

The average proximate composition of wheat (Table 3) compiled from a large number of individual analyses shows that, in common with other cereals, wheat is characterized by relatively low protein and high nitrogen-free extract.

The three principal parts of the wheat kernel and the percentage each constitutes of a well-filled kernel are as follows: (1) endosperm, about 85 per cent; (2) bran or seed coat, 13 to 17 per cent; and (3) germ or embryo, 2 to 3 per cent. The endosperm consists chiefly of starch embedded in a matrix of protein, the bran coat is high in protein, cell-wall constituents and mineral elements, and the germ is high in oil and protein. The chemical composition of the endosperm, bran and germ as found in the various flour streams and by-products of milling are illustrated in Table 4. It may be noted that the lower grades of flour contain larger quantities of ash, protein, and fat, constituents characteristic of bran and germ. This is generally interpreted as indicating progressive contamination of the endosperm with fine particles of the former.

TABLE 7. B VITAMINS IN WHEAT AND MILLING PRODUCTS * 1

	Proportion of Whole Kernel [2] %	Thiamine Content γ/g	Thiamine Proportion of Total %	Riboflavin Content γ/g	Riboflavin Proportion of Total %	Niacin Content γ/g	Niacin Proportion of Total %
Wheat	100.0	5.03	100.0	1.00	100.0	21.08	100.0
Patent flour	63.0	0.68	8.0	0.34	20.5	7.03	22.00
First clear flour	7.0	3.00	3.9	0.62	3.2	17.68	6.14
Second clear flour	4.5	12.37	10.0	1.85	7.7	19.80	4.43
Red dog flour	4.0	29.65	22.0	3.80	14.1	32.41	6.44
Shorts	12.3	17.39	39.6	2.80	32.5	39.29	24.00
Bran	9.0	9.37	15.6	2.80	22.0	68.83	30.66
Germ	0.2	22.93	0.9			63.56	6.31

* Compiled from data of Sherwood et al.,[43] Andrews et al.,[4] and Thomas et al.[47]

[1] Moisture content of samples approximately 11%.

[2] Proportions slightly different in wheat products analyzed for riboflavin.

The commercially important constituents of wheat are starch, protein, and oil. The starch content of a normal wheat kernel varies from 61 to 67 per cent, but it may constitute a lower percentage depending upon its plumpness and its content of protein and moisture.

The protein content of wheat ranges from 6 to 22 per cent. Since quality for the manufacture of various types of wheat products depends to a marked degree on the protein content, considerable attention has been paid to the effect of variety, class, and environment on the protein content of wheat.[3, 9] The true nature and character of the proteins of wheat, especially of gluten, is highly uncertain and indefinite. According to the classical work of Osborne and associates,[10, 11] the principal proteins of the endosperm which form the gluten are a prolamin, *gliadin*, and a glutelin, *glutenin*. The proteins of the germ include an albumin, *leucosin*, a globulin, and proteoses, whereas the bran coat proteins are chiefly a globulin, an albumin, and a prolamin.[27] The nitrogen content of the gluten proteins has been found to be about 17.55 per cent; consequently, in estimating crude protein from determination of total nitrogen the factor 5.7 is commonly used instead of that of 6.25 used for most other foods and feeds. The nutritive or biological value of the wheat proteins which is related to the amino acid composition is of considerable significance since by far the greater part of the product is consumed either as human food or animal feed. The amino acid composition of whole grain, germ, and flour, as well as gluten and gliadin (Table 5) shows that the endosperm proteins are low in the essential amino acids, lysine, and tryptophan, although the whole wheat is higher in these two.

Table 8. Vitamin Content of Cereals and Seeds *

	Carotene		Vitamin A		Thiamine		Riboflavin		Niacin		Pantothenic Acid	
	No. of Samples	Average mg./lb.	No. of Samples	Average IU/lb.	No. of Samples	Average mg./lb.	No. of Samples	Average mg./lb.	No. of Samples	Average mg./lb.	No. of Samples	Average mg./lb.
Barley					59	2.71	16	0.55	15	30.44	14	2.84
Buckwheat					6	2.56	1	0.23	1	20.00		
Corn, white					28	2.22	17	0.61	10	6.04		
Corn, yellow	42	2.20	31	1,990	41	2.06	32	0.60	27	6.40	9	3.36
Oats	29	0.05			28	3.43	10	0.58	8	6.50	6	4.50
Rice, rough					19	1.16	1	0.55	3	13.80		
Rice, brown					14	1.10	1	0.32	4	17.13		
Rice, polished					10	0.26	2	0.36	7	8.08	2	1.82
Rye	4	0.04			18	2.00	9	0.71	9	8.22	1	4.72
Sorghum					11	2.37	2	0.60	3	29.35	2	4.10
Wheat	98	1.15	3	86								
Cottonseed meal	2	0.09	1	54	7	6.13	9	4.08	3	20.40	2	6.35
Linseed meal	3	0.12			6	5.84	3	2.75	2	22.25	1	3.20
Peanuts			1	118	48	3.75	4	1.75	25	60.50	1	15.90
Peanut meal					6	3.27	5	2.35	6	77.50	3	24.10
Soybeans	65	0.38	13	178	16	5.14	7	1.21	7	15.87	1	6.50
Soybean meal	1	0.10			5	2.62	10	1.87	5	17.60	9	6.27

* Compiled from Ellis and Madsen.[20]

The oil or lipid content of whole wheat is about 2 per cent, of the bran 6 per cent, and of the germ 12 to 18 per cent. The characteristics typical of commercial wheat germ have been determined by Sullivan and Bailey:[46] saponification value 184.0; iodine number (Rosenmund) 125.0; thiocyanogen number 84.7; unsaponifiable matter 4.00 per cent; saturated acids 16.0 per cent; hexabromide number 2.28. The percentages of unsaturated constituents in the mixed fatty acids were found to be as follows: oleic 28.14, linoleic 52.31, and linolenic 3.55. Although wheat-germ oil belongs to the class of semidrying vegetable oils, it is higher than most of them in unsaponifiable matter which is particularly high in vitamin E potency, the latter largely accounting for its commercial value.

Data on the average mineral element content of wheat (Table 6) show that the ash, as is the case of other naked cereals, contains a high proportion of potassium, phosphorus, and magnesium, and a low content of calcium. The lack of the latter is important from a nutritive standpoint.

Also nutritionally important is the vitamin content of the foods and feeds prepared from wheat. The distribution of some of the B vitamins in wheat and milling products is presented in Table 7.

These data and others (Table 8) indicate that in comparison with certain other agricultural commodities, wheat is a relatively poor source of vitamins A, C, and D, but a good source of thiamine, riboflavin, niacin, and vitamin E. Since the highest concentrations of most of these vitamins occur in the germ and outer parts of the kernel, high proportions are discarded in the production of white flour.

CORN

Corn (*Zea mays*) is a warm weather plant requiring high temperatures both day and night during the growing season. Greatest production is obtained with a growing season of 140 or more days and with mean summer temperatures of 75° F. and night temperatures exceeding 58° F. Other environmental requirements for optimum growth and grain production are abundant sunshine and a plentiful supply of moisture well distributed throughout the growing season. Although these conditions are required for maximum production, corn has a great environmental adaptability and is grown under a wide range of temperature and rainfall conditions.

The world production of corn averages approximately 4721 million bushels[5] (Table 1). The United States produces more than half of this total. In this country, commercial production of corn centers in the so-called Corn Belt, the fertile prairie soils extending from Ohio westward and northward. Of the five general types of corn—dent, flint, pop, flour, and sweet—the first two are of greatest commercial importance. Dent is the type largely grown in the United States, constituting more than 90 per cent of the total production. In Argentina, the world's second largest corn producer, the reverse is the case with the flint type representing about 99 per cent of the total production. In recent years the development and use of hybrid corn (the first-generation cross or hybrid involving two or more inbred strains of corn) has resulted in spectacular increases in yield and important improvements in quality of corn for specific uses. Of possible future commercial importance are the hybrids into which has been introduced the waxy starch character. This type of starch, which has properties corresponding more nearly to the starches from root crops such as cassava from which tapioca is prepared, is characterized by staining reddish-brown with iodine rather than blue.

The 2608 million bushels of corn produced in the United States annually (1935–44) were utilized as shown in Table 9.

TABLE 9. DISPOSITION OF COMMERCIAL CORN IN THE UNITED STATES, 1935–44 *

Use	Amount Consumed Annually, 1000 bushels	% of Total Production
Feed, other uses, waste	2,346,632	90.0
Seed	14,505	0.6
Dry process products		
Breakfast foods	8,818	0.3
Farm household use	25,980	1.0
Corn meal, grits, etc.	47,280	1.8
Wet process products		
Starch, syrup, sugar, etc.	97,422	3.7
Alcohol and distilled spirits	29,229	1.1

* Compiled from Agricultural Statistics.[5]

As shown above, the principal use of corn is as livestock feed. Three substances of commercial importance can be separated from the corn kernel—starch, protein, and oil. Industrial use of corn, confined largely to the starch fraction, is in two fields: (1) production of starch or starch derivatives and products associated therewith, and (2) production of alcohol, alcoholic products, or organic acids. Most of the starch or starch derivatives are produced by the "wet-milling" process in which the protein associated with corn by-products is returned to the farm as feed while the oil is an industrial by-product. An idea of the diversity of the products made from wet-milled corn and their uses can be gained from Table 10.

The average proximate composition of corn (Table 3) indicates that, compared with wheat, corn is low in protein, fiber, and ash but relatively high in oil. The corn kernel consists of three distinct parts—endosperm, germ, and pericarp or bran. The relative proportions of the three component parts and the chemical composition of each have been determined by Earle, Curtis, and Hubbard[19] as shown in Table 11.

The results show that the endosperm contains approximately 16 per cent of the total ash, 75 per cent of the total protein, 15 per cent of the oil, 28 per cent of the sugar, and 98 per cent of the starch, whereas the germ contains approximately 80 per cent of the total ash, 22 per cent of the protein, 84 per cent of the oil, and 70 per cent of the sugar.

Table 10. List of Products Made from the Corn Kernel in Corn-Refining Plants *

Starches	Dextrins	Syrups	Sugars	Corn Oil	Feeds	Miscellaneous
Pearl Powdered Thick boiling Thin boiling Soluble Alkaline Chlorinated Non-congealing Gelatinized Binder Crystal Lump Bakers' Boraxed Confectioners' Brewers' grits	Canary dextrin White dextrin Special dextrins British gum Special gums Founders' mixture	Mixing corn syrup Special tanners' corn syrup Brewers' corn syrup	Dextrose, chemically pure Refined corn sugar Refined hydrate corn sugar Refined bread sugar Corn sugar seventy Corn sugar eighty	Corn oil, crude Corn oil, refined Corn oil, solidified Soap stock Solid soap Black grease	Corn gluten feed Corn gluten meal Corn oil cake meal Corn bran	Lactic acid Zein Calcium lactate Pudding powders Corn sugar molasses [Hydrol] Yeast Sodium lactate
			----- And Their Uses			
Textiles Paper Confectionery Household Baking Baking powders Brewing Asbestos Explosives Laundry Pastes Sizings Soaps Cosmetics Pharmaceuticals	Textiles Paper Colors Carpets Twine Window shades Pastes Sizings Gums Glues Mucilage Leather Fireworks	Confectionery Ice cream Preserves Table syrups Food sauces Canned meats Jams, jellies Baking Beverages Brewing Tobacco Pharmaceuticals	Caramel Sugar color Brewing Vinegar Ice cream Dietetics Pharmaceuticals Fibre Silk [Rayon]	Textiles Salad and cooking oil Soaps Commercial Baking Pharmaceuticals	Beef cattle Dairy cattle Sheep Poultry Other domestic animals	Dietary Medical Experimental Foods Tanning

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While available information indicates that little material difference in composition of corn can be attributed to climate, Hopkins et al.[24] found that large differences could be produced by selection. Starting with one variety and by selection based on analysis, in seven years they produced high and low protein and high and low oil strains. Kernels of the four strains separated into their component parts for analysis showed that a higher protein content in the endosperm accounted for most of the difference between the high and low protein; while the increased content of oil was accounted for by a higher oil content of the embryo.

TABLE 11. COMPOSITION OF CORN FRACTIONS *
(MOISTURE-FREE BASIS)

Part	Proportion of Whole Grain %	Ash %	Protein [Nx6.25] %	Oil %	Sugar %	Starch %
Endosperm	81.9	0.31	9.4	0.8	0.64	86.4
Germ	11.9	10.10	18.8	34.5	10.81	8.2
Bran	5.3	0.84	3.7	1.0	0.34	7.3
Tip cap [1]	0.8	1.59	9.1	3.8	1.61	5.3

* Data from Earle et al.[19]
[1] Loose chaffy tissue at base of kernel.

The principal protein of corn, the prolamin *zein*, accounts for over half of the crude protein content; somewhat less abundant is a glutelin. The amino acid composition of whole kernels, corn germ, gluten, and zein are summarized in Table 5. Corn oil belongs to the semidrying class, and in the United States most of it is refined for edible purposes such as salad and cooking oils as well as in the manufacture of some lard substitutes. The characteristics of a sample of "dry process" corn oil determined by Baughman and Jamieson [12] were as follows: specific gravity at 25°/25° C. 0.9185; refractive index (20° C.) 1.4717; iodine number (Hanus) 117.2; saponification value 187.3; acetyl value 10.0; acid value 2.5; unsaponifiable matter 1.72 per cent (iodine no. 113); saturated acids 11.2 per cent and unsaturated acids 83.3 per cent (iodine no. 137.2). The oil contained the following percentages of acids: oleic 43.4, linoleic 39.1, palmitic 7.3, stearic 3.3, arachidic 0.4, and lignoceric 0.2.

The mineral element composition of corn (Table 6) differs from that of other cereals principally in an unusually low content of calcium. The vitamin content of corn is of importance due to the large quantity of this grain used as feed and food. Compared to other grains (Table 8) yellow corn is relatively rich in provitamin A as well as vitamin A. Appreciable quantities of thiamine and riboflavin are present, but this cereal is a poor source of niacin.

BARLEY

Barley (*Hordeum distichum* and *H. vulgare*) is one of the most ancient of cultivated plants. One of the distinctions of this grain is that it is grown farther north than any other cereal crop. Barley may be grown from either spring or fall seeding. It may be classified also on the basis of the number of rows of kernels on a head; thus it may be 2-rowed or 6-rowed. In general, the climatic requirements for barley are similar to those for wheat. The United States production is about 10 per cent of the world's estimated production of 2338 million bushels (Table 1), and is concentrated mainly in the Dakotas and Minnesota and in California.

Barley is grown primarily as feed for livestock; malting barley brings better prices, but production for this purpose is limited to areas of moderately high rainfall because the grain must be characterized by mellowness, occasioned by a high starch content, capable of yielding a high percentage of extract, and a moderate protein content. A review of the earlier literature on this subject is given by Le Clerc and Wahl.[35] Out of an average annual United States production, 1935–45, of 289,598,000 bushels,[5] 73,441,800 bushels were used for malting, 94.0 per cent of this being used for alcohol and alcoholic beverages. Another food use for a small quantity is as pearl barley.

The average proximate composition, mineral element and vitamin contents of barley are given in Tables 3, 6, and 8. Since this is one of the cereals with hulls, it is characterized by higher crude fiber and ash contents than the naked cereals. The ash had the highest iron content of the cereals.

Osborne[39] considered that the proteins of barley consisted of a prolamin, *hordein*, a globulin, *edestin*, albumin, *leucosin*, a proteose, and a glutelin.

OATS

Oats (the principal cultivated species being *Avena sativa*) are essentially a crop of moist temperate regions. They are primarily a European and North American crop, production in the United States accounting for nearly one-fourth of the world total (Table 1). In the United States and Canada oats rank second only to wheat in importance among small grains. The principal region of production is a broad irregular band extending from New England to North Dakota; the area of greatest concentration coincides very closely with the center of the Corn Belt.

The great bulk of the oat crop is used for feeding livestock. About 3 per cent, 1100 million pounds,[5] of the total crop is consumed as breakfast cereals, making oat milling the leading industry in the production of this product. Small quantities of oat flour are also used as an antioxidant in the food industry.

Data on average proximate composition, amino acid content, mineral element content and vitamin content of oats are presented in Tables 3, 5, 6, and 8. From a nutritive standpoint the characteristics which make this grain valuable for feed and food are that it is the highest of the cereals in fat and ash, high in protein and crude fiber, high in calcium and iron, and rich in thiamine. It is, however, relatively low in niacin.

The proteins of oats are not so well understood as are those of wheat and corn; but they are thought to consist principally of a globulin, *avenalin,* a gliadin and a glutelin, *avenin.* In contrast with corn in which the prolamin is the chief protein, oats are low in prolamin, the glutelin comprising the bulk of the protein.

RYE

Rye (*Secale cereale*) is characterized by being the most winter-hardy of the cereals and by its ability to grow under adverse conditions. While this grain is the world's second most important bread crop it is of minor importance in the United States which produces less than 3 per cent of the world crop (Table 1). Formerly grown principally in Michigan, Wisconsin, and Minnesota, it is now produced largely in the northern Great Plains and to a lesser extent in the central and southern Great Plains.

Of an average annual United States production (1939–44) of 39,589,166 bushels,[5] 62.2 per cent was used for feed, 15.2 per cent for spirits and alcohol, and 19.7 per cent for food. The 1939 census showed a production of 280,416,000 pounds of rye flour valued at slightly over 4 million dollars. Rye bread is produced in this country from a mixture of rye and wheat flours. In feeding, rye is also usually mixed with other grains because of its unpalatability.

A by-product of rye of considerable commercial importance is *ergot,* the sclerotia of the fungus *Claviceps purpurea.* The hard, dark-colored, hornlike bodies that replace the normal kernels in the head contain a series of physiologically active alkaloids used for medicinal purposes. Because of its poisonous nature the ergot must be removed before milling or feeding.

Rye and wheat are similar in structure and composition; this applies not only to group analyses but to the nature and characteristics of the components of the groups. The average proximate composition for rye in comparison with other grains is given in Table 3. The chemical composition of rye flours of different grades or extractions is presented in Table 12.

The data show that rye is similar to wheat in general composition and furthermore, that the percentages of protein, fat, fiber, thiamine, riboflavin, and ash increase and the percentage of starch decreases with increasing percentages of extraction.

The principal distinction of rye from wheat is the failure of the former to yield gluten on washing dough which undoubtedly accounts for the inferior baking properties of rye flours. After reviewing the works of Osborne, Csonka, and Jones and others regarding the proteins of rye, Winton and Winton[51] conclude that, although the gliadins of rye and wheat appear identical, their glutelins possibly are not.

TABLE 12. CHEMICAL COMPOSITION OF RYE FLOUR OF DIFFERENT MILLING EXTRACTIONS FROM ENGLISH RYE *

Part I

Extraction Rate %	Protein [Nx5.7] %	Fat %	Starch %	Fiber %	Thiamine IU/g.	Riboflavin γ/100g.
100	7.98	1.98	69	1.56	1.45	2.90
85	7.30	1.64	73	0.84	0.98	2.00
75	6.67	1.33	75	0.48	0.80	1.40
60	5.64	1.01	78	0.22	--	0.85

Part II

Extraction Rate %	Ash %	K	Ca	Mg	Fe	Total P
		mg./100 g.		mg./100 g.	mg./100 g.	
100	1.72	412	31.5	92	2.70	359
85	1.04	203	26.1	45	1.97	193
75	0.72	172	19.5	26	1.72	129
60	0.51	140	15.3	16	1.32	78

* Compiled from McCance et al.[36]

The mineral element composition of rye (Table 6) is characterized by relatively high potassium and calcium contents, the latter being the highest of any of the cereals listed. In vitamin content (Table 8) rye is similar to oats in being low in carotene compared with wheat or corn, contains moderate amounts of thiamine and niacin, and is somewhat higher in riboflavin and pantothenic acid than any of the other cereals.

RICE

Climates in which rice (*Oryza sativa*) is grown are characterized by high temperatures during the growing season, an abundance of moisture and, in most instances, a high atmospheric humidity. Most of the world production is in the Far East, the United States producing less than 0.7 per cent of an average annual world production of nearly 7.5 billion bushels (Table 1). The three principal producing areas in the United States are the broad level prairies of southwestern Louisiana, southeastern Texas, eastern Arkansas, and the Sacramento and San Joaquin valleys of California. Cultivated varieties are of two types—upland and lowland. The former is grown without irrigation; the latter is flooded for 60 to 90 days during the growing season. Upland rice is relatively unimportant. The crop grown in the United States is entirely lowland rice and includes varieties of the long, medium, and short grain types.

About 90 per cent of the rice produced in the United States is milled, only about 1 per cent being consumed as feed. The process of milling rice differs fundamentally from the milling of wheat in that with wheat fine flour is the end product whereas with rice whole grains are desired.

TABLE 13. AVERAGE CHEMICAL COMPOSITION OF CULTIVATED RICE AND ITS BY-PRODUCTS *

Product	Proximate Composition						Sugars		Pentosans
	Moisture %	Protein %	Fat %	Fiber %	N-free Extract %	Ash %	Reducing %	Disac-charide %	%
Rice:									
Rough rice	11.7	8.1	1.8	8.9	64.5	5.0	--	--	--
Brown rice	12.2	9.1	2.0	1.1	74.5	1.1	0.1	0.8	2.1
Head rice	12.6	9.0	0.5	0.4	77.0	0.5	0.1	0.2	1.8
Second head rice	12.4	8.7	0.4	0.4	77.4	0.7	0.1	0.2	1.9
Screenings rice	11.4	8.4	0.5	0.4	78.7	0.6	Tr.	0.3	1.8
Brewers' rice	11.8	8.9	1.0	0.6	77.1	0.7	0.2	0.2	1.7
By-products									
Stone bran	9.7	9.8	7.7	20.9	36.7	15.2	0.8	1.2	13.9
Huller bran	9.8	15.0	16.9	7.9	42.0	7.4	1.2	4.5	7.8
Cone bran	9.8	15.4	16.0	5.7	46.1	7.1	1.6	2.2	5.8
Polish	9.9	12.9	9.1	2.1	61.8	4.2	1.3	2.3	3.5
Hulls	8.5	3.6	0.9	39.1	29.4	18.6	0.2	0.4	18.1

* Compiled from Fraps.[21]

The important steps in the milling process are: (1) removal of the hulls from the rough rice by means of hulling stones, the resulting product called "brown" rice consisting of the bran coats and seed proper; (2) removal of the bran coats and germ in hullers, and (3) polishing the remaining whole endosperms in a "brush."

The polished endosperms are boiled and consumed mostly as a vegetable, with small quantities being used as breakfast cereals. By-products of the milling process are the broken kernels (utilized as human food, feed for animals, in brewing and as flours), rice bran and rice polish, which are valuable cattle feeds, and the rice hulls which serve for packing and various technical purposes.

The average proximate composition of rice (Table 3) differs from that of other cereals in being low in fiber and ash, and high in nitrogen-free extract. According to analyses cited by Winton and Winton,[51] climate, type, and varieties have relatively little effect on the protein content of rice. The relative chemical composition of the various mill products produced by Texas milled rice as reported by Fraps[21] are presented in Table 13.

The data show that the process of removing the hulls in producing brown rice results in an increase in protein and nitrogen-free extract, and a marked decrease in fiber and ash. The process of removing the bran layers and germ in the production of polished rice results in marked decreases in fat, fiber, and ash, and a slight increase in protein. The by-product rice bran is relatively high in protein, fat, and ash, whereas the rice polish is somewhat lower in protein and ash but much higher in nitrogen-free extract.

TABLE 14. B COMPLEX VITAMINS IN RICE AND ITS MILL PRODUCTS (MOISTURE-FREE BASIS) *

Product	Thiamine γ/g.	Riboflavin γ/g.	Niacin γ/g.	Thiamine γ/g.	Niacin γ/g.	Pantothenic acid γ/g.	Pyridoxine γ/g.
Rough rice	2.93	0.67	49.2	--	--	--	--
From milling process:							
Brown rice	3.02	0.53	55.1	4.2	47.2	17.0	10.3
Finished white rice:							
Head rice	0.60	0.26	18.4	0.8	12.7	6.4	4.5
Second head rice	0.50	0.25	17.7	--	--	--	--
Screenings	0.79	0.34	23.8	--	--	--	--
Brewers' rice	1.41	0.36	36.1	--	--	--	--
By-products;							
Hulls	1.11	0.76	18.6	--	--	--	--
First break bran	27.33	2.68	332.0	27.9	408.6	71.3	32.1
Second break bran	17.86	1.77	286.3				
Pearling cone polish	22.88	1.62	367.8	23.3	384.7	92.5	30.8
Brush polish	20.96	1.34	290.4				

* Data for first three columns are averages of seven mill lots.
Data for last four columns are averages for composite samples of three varieties.
Compiled from data of Kik et al.[29, 31, 32], and Williams et al.[50]

The bulk of the protein of rice consists of the glutelin, *oryzenin*, with small quantities of globulin and albumin and little prolamin. The amino acid content of rice protein is presented in Table 5.

Rice bran contains from 8 to 16 per cent of oil, depending on its source. It is a semidrying oil and is used, after refining, for edible purposes. The characteristics of an oil extracted by ether from American rice bran as given by Jamieson[25] follow: iodine number (Hanus) 99.9; saponification value 185.3; unsaponifiable matter 4.64 per cent; acid value 73. The oil contained the following percentages of acids; oleic 39.2, linoleic 35.1, myristic 0.5, palmitic 11.7, stearic 1.7, arachidic 0.5, and lignoceric 0.4.

The mineral element composition of rice (Table 6) is characterized by a very low iron content. Average data on the B-complex vitamins are given in Table 8, and more recent studies by Kik and associates[29, 31, 32] and R. Williams[50] are summarized in Table 14. The latter data show that, whereas the first step in the milling process (the change from rough to brown rice) has little effect on the vitamin content, the subsequent processing to polished rice removes about 80 per cent of the thiamine, 50 per cent of the riboflavin, 65 per cent of the niacin, 62 per cent of the pantothenic acid, and 50 per cent of the pyridoxine. Because of the nutritional significance of this loss in milling, methods for retaining more of these vitamins have received considerable attention. One approach to the problem has been to try to leave more of the vitamin-rich bran and germ on the grain in milling (a process called "undermilling"), while another has been to transfer the vitamins to the endosperm by parboiling or other means prior to milling. That some of these processes have considerable merit in retaining the vitamins has been shown by Kik[30] who found that the most efficient method ("converted" rice) retained as much as 91.4 per cent of the thiamine, 83.3 per cent of the riboflavin, and 81.7 per cent of the niacin found in brown rice.

BUCKWHEAT

Although buckwheat (*Fagopyrum esculentum*) does not belong to the grass family it is classed with the cereals because it is used for food. This grain is a short season crop, growing in moist, cool climates, and is particularly tolerant of poor soil conditions. The United States, with an average annual production[5] of slightly less than 7 million bushels, ranks fifth in world production, with Russia the largest producer and France second. In the United States principal production is in the states of Pennsylvania and New York.

Approximately 60 per cent of the buckwheat produced in the United States is fed to livestock;[5] of the remainder only about 2.5 per cent is ground for home use or exchanged for flour. The principal use of milled buckwheat is in pancake flour.

The proximate composition of buckwheat (Table 3) shows that the whole grain resembles oats in being relatively high in fiber and low in nitrogen-free extract but is lower than oats in fat and ash. Analyses of buckwheat and its mill products are presented in Table 15.

The data show that whereas low extraction flours are low in protein, fat, and fiber, and high in nitrogen-free extract, increasing percentages of extraction in the milling process are accompanied by increases in percentage of constituents highest in the bran layers and germ—i.e., protein, fat, fiber, and ash, as has also been shown to be true in the milling of wheat and rye.

TABLE 15. COMPOSITION OF BUCKWHEAT AND BY-PRODUCTS DERIVED THEREFROM * (MOISTURE-FREE BASIS)

Product	Ash %	Fat %	Protein %	Fiber %	N-free Extract %
Grain	1.92	2.64	12.15	13.59	69.69
Groats [whole]	2.07	3.24	14.82	1.07	78.81
Flour					
Very light	0.70	0.57	5.41	0.45	92.87
Light	1.40	1.86	8.91	0.68	87.15
Medium	1.56	2.10	11.09	1.09	84.16
Dark	1.71	2.76	15.65	1.15	78.73
Very dark	2.09	3.31	15.57	1.44	77.59
Hulls	1.83	0.91	2.82	56.03	38.75

* Data are averages for three varieties—Japanese, Silverhull and Tartary. Compiled from Coe.[18]

Little information is available on the mineral and protein composition of buckwheat. Data on B-complex vitamin contents are given in Table 8.

SORGHUM

Reliable statistics are not available on world production, but sorghum (*Sorghum vulgare*) is grown extensively in northern China, Manchuria, India, and widely distributed in Africa. Areas in the United States in which sorghum is grown extensively are those which are too hot and dry for successful corn growing, and include Texas, Oklahoma, Kansas, and Nebraska. While the average annual United States production,[5] 1936–45, was 90,341,800 bushels, there has been a steady increase in production from about 30 million bushels in 1936 to over 100 million in 1941.

Of the four classes of sorghum—sweet grass, broomcorn, sorgo, and the grain sorghum—the last two named are of greatest interest. In the United States the grain sorghums have been utilized largely as feed for livestock, although small quantities are used in pancake flours and breakfast foods. Certain varieties of sorghums yield the so-called waxy starch which has properties similar to those of tapioca and sweet potato starches and thus may compete with waxy corn.

The proximate composition of sorghum grain (Table 3) closely resembles that of corn. The chemical composition and starch yield of several grain sorghums as determined at the Kansas Agricultural Experiment Station are summarized in Table 16.

TABLE 16. CHEMICAL COMPOSITION OF SORGHUM GRAINS *

	Kaffir Types[1] %	Glutinous Types[2] %	Miscellaneous Types[3] %
Moisture	10.40	12.72	10.13
Ash	2.17	2.30	1.97
Protein	13.88	12.19	14.45
Crude fat	3.97	3.73	3.64
Crude fiber	1.97	3.87	1.77
Reducing sugars, as maltose	0.33	0.33	0.30
Nonreducing sugars, as sucrose	1.20	0.69	1.19
Starch	64.60	58.40	64.68
Starch yields	52.7	45.2	51.5
Tannin	0.0295	0.1583	0.0065
P	0.482	0.378	0.431
Mn [$x10^3$]	1.6	1.3	1.4
Fe [x10]	0.107	0.101	0.101
Na	0.023	0.027	0.017
Cu [$x10^3$]	0.83	2.00	0.82

* Taken from Barham et al.[11]

[1] Average of seven varieties.

[2] Average of two varieties.

[3] Average of five varieties.

The relative proportions of bran, corneous and starchy endosperm, and germ and the chemical composition of each as reported by Bidwell et al.[14] for three varieties are presented in Table 17.

TABLE 17. PROPORTIONS OF COMPONENT PARTS OF SORGHUM AND CHEMICAL COMPOSITION OF THE KERNEL AND ITS PARTS [1]

Component Part of Kernel	Proportion of Kernel %	Ash %	Ether Extract %	Protein %	Crude Fiber %	N-free Extract %	Starch %
Whole grain	100	1.83	3.54	14.46	1.98	78.19	64.86
Bran	6.1	2.67	5.62	6.24	15.04	70.42	2.75
Corneous endosperm	54.9	0.52	0.39	16.45	1.17	81.46	27.13
Starchy endosperm	29.6	0.66	0.57	10.39	1.33	89.05	76.25
Germ	9.5	11.34	25.62	20.61	7.15	35.28	1.85

[1] Average of data reported for three grain sorghum varieties.

[2] Compiled from Bidwell et al.[14]

The results show that the percentages of bran, germ, and endosperm obtained from sorghum were similar to those from corn, the two grains differing principally in a much greater yield of ether-extractable material from sorghum bran. More recent studies [33] of the ether-extractable material in the bran and oil meal have shown that it consists of about 6 per cent of a wax with characteristics similar to carnauba wax, and about 8 per cent of an oil similar to corn oil.

Like corn, the bulk of the protein content of sorghum consists of a prolamine. The content of B-vitamins (Table 8) is similar to corn except in niacin which is much higher in sorghum.

COTTONSEED

Although cotton (*Gossypium herbaceum*) is grown primarily for fiber, the crop produces a series of valuable by-products, one of the most important being cottonseed. The average annual world cottonseed production 1935–39 (Table 1) was about 15 million tons, of which the United States produced a little over one-third. Of the 5,143,000 tons produced annually in the United States, 1936–45,[5] 4,382,000 tons were crushed, with the production of 1371 million pounds of oil, 1,969,000 tons of cake and meal, and 1,086,400 tons of hulls. Thus nearly all the cottonseed produced in this country, except what is saved for seed, is processed for the production of oil, the cake and hulls constituting valuable by-products for livestock feed.

TABLE 18. PROXIMATE COMPOSITION OF COTTONSEED AND DERIVED PRODUCTS * (MOISTURE-FREE BASIS)

Constituent	Whole seed %	Kernels %	Hulls %	Meal or cake %
Moisture	9.9	6.9	9.3	7.8
Oil	19.5	29.6	0.9	7.4
Protein [Nx6.25]	19.4	30.3	3.8	44.8
Crude fiber	22.6	4.8	46.1	9.9
Ash	4.7	6.9	2.6	5.6
N-free extract	23.9	15.4	37.3	24.5

* Data from Guthrie et al.[23]

In obtaining the oil by pressing, the seeds are first delinted, then cracked and the hulls separated from the decorticated seeds by screening. According to Jamieson [25] the oil is utilized for various purposes as follows: shortenings 72 per cent, cooking and salad oils 11 per cent, margarine 7 per cent, and soap 11 per cent.

Cottonseed varies in composition according to variety, climate, soil and other factors. Proximate composition data (Table 3) show that on the average the percentages of oil and protein are about equal, both being somewhat less than the percentage of nitrogen-free extract. The meats or kernels are considered to constitute slightly over half of the seed, most of the remainder being hull. Data on the average approximate composition of cottonseed and derived products compiled by Guthrie et al.[23] are presented in Table 18.

The oil obtained from cottonseed is classified as semidrying. Information on its composition and characteristics are presented in Tables 19 and 20. The component fatty acids consist largely of the unsaturated acids linoleic and oleic, and the saturated acid palmitic. Other substances present in the oil as minor constituents are tocopherols and sterols.

TABLE 19. COMPOSITION AND PROPERTIES OF VEGETABLE OILS *

	Peanut	Cottonseed	Soybean	Linseed
Oleic [%]	50.6-71.5	22.9-33.15	21.0-33.6	21.7-37.6
Linoleic [%]	13.0-26.0	39.35-47.8	49.3-58.8	3.3-23.1
Linolenic [%]			2.2-8.1	25.7-58.3
Myristic [%]		0.3-2.1		
Palmitic [%]	6.0-8.5	19.1-23.4	6.5-9.7	3.8-6.9
Stearic [%]	2.6-6.0	1.1-2.9	2.4-4.4	2.2-4.8
Arachidic [%]	2.6-4.9	0.1-1.3	0.7-0.9	0.22-0.86
Lignoceric [%]	2.5-3.0		0.1	0-0.36
Unsaponifiable matter [%]	0.2-0.3	0.9	0.6	0.6-1.6
Smoke point [°F.]	464	508	492	320
Fire point [°F.]	692	644	673	680
Flash point [°F.]	632	582	618	588
Iodine value	83-95	103-115	103-152	170-204
Normal iodine value	90	109	130	180

* Compiled by Alderks.[1]

Studies of the proteins in cottonseed have been complicated by the oil, resins, and coloring matter present. Two globulins, α and β, were found by Jones and Csonka[28] to comprise 2.59 and 15.0 per cent, respectively, in the meal, together with smaller quantities of a pentose protein, two phospho-proteins and glutelin. The amino acid composition of cottonseed protein is given in Table 5.

The carbohydrates present in cottonseed consist largely of the trisaccharide *raffinose*, and the cell wall constituents cellulose, hemicellulose, and pectinlike substances.

The vitamin content of cottonseed meal, Table 8, characterizes it as a poor source of vitamin A, a good source of thiamine and riboflavin, and a fair source of niacin and pantothenic acid.

One of the unique constituents of cottonseed is the pigment *gossypol*, a phenolic compound which occurs to the extent of 0.4 to 1.2 per cent in the kernels and hulls and averages about 0.05 per cent in crude cottonseed oil. In its "active" form gossypol has toxic physiological effects but in modern pressing methods which include the use of heat, the gossypol is rendered inactive and the commercial meal and cake are nontoxic feeds.

TABLE 20. VALUES OF COMMON EDIBLE OILS *

	Sp. gr. 15.5° C.	Ref. Index 25°C.	Hebner No.	Sapon. No.	Iodine No.	Maumené No.	Reichert-Meissel No.	Acetyl No.	Fatty Acids, Titer	Unsaponifiable Matter
Cottonseed									°C.	%
Min.	0.922	1.470		191	104	50	0.7	21.0	34	0.7
Max.	0.925	1.472		195	114	78	0.9	25.0	40	1.7
Linseed										
Min.	0.931	1.4782	95.0	190	170	90	0.0	3.9	19	0.5
Max.	0.938	1.4825	95.5	196	202	145			21	2.0
Peanut										
Min.	0.911	1.4707	95.0	186	83	44	0.5		23	0.5
Max.	0.926	1.4731	96.0	189	105	51			32	1.0
Soybean										
Min.	0.9207	1.4710	95.5	190.1	115	60				0.2
Max.	0.9310	1.4750		197.4	145	88				0.2

* Reprinted by permission from "The Structure and Composition of Foods" by A. L. Winton and K. B. Winton, published by John Wiley & Sons.[51]

FLAXSEED

Argentina is the world's greatest producer of flaxseed (*Linum usitatissimum*), United States production accounting for only about 8 per cent (Table 1). The present principal seed-flax producing area coincides very closely with that of spring wheat, extending slightly further east, with minor production in California and Texas. The crop is spring-sown in the former area and fall-sown in the latter two states.

Seed flax is a cash crop, practically all the crop being sold for crushing except that saved for seed. The average annual production of linseed oil for the 10-year period 1936–45 was nearly 700 million pounds, with 640,700 tons of linseed cake and meal as by-products. The oil is obtained either by expressing (old process) or solvent extraction (new process), the former leaving about 5 per cent more oil in the meal than the latter. Linseed oil has long been the most important source of drying oil in the paint and varnish industry and is also used extensively in the manufacture of linoleum, oilcloth, printer's ink, patent and imitation leather. The linseed cake and meal are highly valued as feed.

The proximate composition of flaxseed in comparison to other oil seeds is given in Table 3 and the percentage composition of hull and embryo fractions in hand-decorticated flaxseed as found by Smith et al.[45] is presented in Table 21.

TABLE 21. PERCENTAGE COMPOSITION OF HULL AND EMBRYO FRACTIONS IN HAND-DECORTICATED FLAXSEED *

	Whole Seed	Embryo	Hull
Moisture	7.13	4.31	7.89
Nitrogen	4.01	4.64	3.18
Oil	38.7	53.20	1.84
Ash		3.38	2.99
Weight %		58.60	41.40
% of total oil in:		96.7	3.3

* Data from Smith et al.[45]

The composition and properties of linseed oil (Tables 19 and 20) show that the oil is characterized by a very high iodine value due to the content of acids of a higher degree of unsaturation than oleic.

The protein of linseed has been investigated by Osborne [38] who isolated a crystalline globulin, an albumin, a protein resembling both albumin and globulin, a proteose, peptone-like bodies, and a glutelin. These accounted for only about 3.5 per cent of the total of 8.40 per cent. Recently Vassel and Nesbitt [49] isolated and named *linin,* a protein which they considered the major protein of linseed meal; a second protein, *conlinin,* was found to be present in smaller amounts.[48] The amino acid composition of linseed meal (Table 5) is characterized by comparatively high tyrosine and valine contents.

The content of vitamins in linseed meal and of minerals in the seed are given in Tables 6 and 8. This seed is similar to cottonseed in being a good source of some of the B-vitamins but is relatively low in the minerals potassium, phosphorus, and sulfur.

PEANUT

The peanut (*Arachis hypogaea*) which is a pea rather than a nut, is strictly a warm season crop, grown only in the warmer parts of the temperate zone and tropical or subtropical climates. The United States produced a little less than 7 per cent of the estimated average world crop for the period 1935–39 (Table 1), the greatest production being in the states of Virginia, North Carolina, Georgia, and Alabama, and some in other southern states as far west as Texas.

A considerable portion of the peanut crop is used for the production of peanut oil, the by-product meal being used for livestock feed and to a minor extent as fertilizer. Of an average annual, 1936–45, production[5] of 1747 million pounds picked and threshed, 290 million pounds were crushed with the production of 106,711,000 pounds of crude peanut oil and 168,030,000 pounds of cake and meal. The oil may be obtained by either the hydraulic or expeller process. Farm disposition (seed, feed, and farm household use) also accounts for rather large portions of the crop. Small quantities of the crop are consumed in other food forms, as roasted and salted nuts and peanut butter.

The average proximate composition of peanut kernels (Table 3) indicates a very high oil content (about 50 per cent), a high protein content but low fiber, nitrogen-free extract and ash contents.

The oil obtained from the peanut is classified as nondrying and is used chiefly in the manufacture of vegetable margarine, with lesser proportions used as salad and cooking oils, in vegetable shortenings and in soap. The composition and properties of the oil given in Tables 19 and 20 show a much higher proportion of oleic than linoleic acid, with smaller proportions of palmitic, stearic, arachidic, and lignoceric acids. The unsaponifiable matter content is lower than in the oils from the other seeds listed.

Two globulins, *arachin* and *conarachin*, were found by Johns and Jones[26] to comprise the bulk of the peanut protein. The approximate percentages of amino acids in peanut flour are presented in Table 5. These values as well as miscellaneous feeding studies show that peanut protein is an excellent source of the essential amino acids.

General analyses indicate that the carbohydrate content of peanut kernels is relatively low, sugars and starch constituting most of the nitrogen-free extract. The vitamin content of peanut meal (Table 8) is characterized by high levels of niacin and pantothenic acid and adequate levels of thiamine and riboflavin.

SOYBEANS

The soybean (*Soja max*) is a summer leguminous annual, grown both for forage and for seed. It has a wide range in adaptation. In general, soil and climatic conditions favorable to corn are also well suited to soybeans. The United States ranked third in production of this crop (Table 1), China ranking first and Manchuria second. In the same period the average annual production of the United States was about 12 per cent of the world production. The most important areas of production in the United States are the central portions of the Cotton Belt and the Corn

Belt, seed production centering in the states of Illinois, Iowa, Ohio, Indiana, and Missouri. In these states especially there have been marked increases in production in the last few years.

TABLE 22. OUTLINE OF SOYBEAN UTILIZATION

- Soybeans
  - Plants
    - Forage
      - Ensilage
      - Fuel
      - Furfural
      - Hay
      - Silage
    - Green manure
    - Pasture
  - Beans
    - Defatted meal
      - Emulsifier
      - Core binder
      - Feeds
        - Cattle
        - Dogs
        - Fish
        - Hogs
        - Poultry
        - Rabbits
        - Sheep
      - Fertilizer
      - Glue
      - Human food
        - Grits
        - Beer brewing
        - Flour [see whole beans]
        - Seasoning powders
        - Soy sauce
        - Vegetable milk
      - Plastics
      - Industrial protein
        - Paints
        - Paper size
        - Textile dressing
        - Waterproofing
    - Oil
      - Candles
      - Celluloid
      - Core oil
      - Disinfectant
      - Electrical insulation
      - Enamels
      - Food products
        - Dip coatings
        - Margarine
        - Cooking oils
        - Shortening
        - Salad oils
        - Medicinal oil
      - Fuel
      - Glycerin
      - Insecticides
      - Lecithin
        - Cocoa
        - Emulsifier
        - Margarine
        - Medicines
        - Textile dyeing
        - Candy
        - Chocolate
        - Gasoline stabilizer
      - Lighting
      - Linoleum
      - Lubricant
      - Oilcloth
      - Paints
      - Printing ink
      - Rubber substitutes
      - Soaps
        - Hard
        - Liquid
        - Soft
      - Synthetic resin
      - Varnishes
      - Waterproof for cement
      - Waterproof goods
    - Green beans
      - Canned
      - Frosted
      - Green vegetable
      - Salad
    - Whole beans
      - Feeds
        - Cattle
        - Hogs
        - Poultry
        - Sheep
      - Baked
      - Boiled
      - Flour
        - Baked products
        - Breakfast foods
        - Candies
        - Chocolate
        - Diabetic foods
        - Health drinks
        - Ice cream cones
        - Ice cream powder
        - Infant foods
        - Macaroni products
        - Meat products-filler
      - Breakfast foods
      - Roasted
        - Candied
        - Coffee substitutes
        - Salted
      - Grits
      - Soy sauce
      - Sprouts
      - Vegetable milk
        - Casein
        - Condensed
        - Foods
        - Curd
          - Canned
          - Dried
          - Fermented
          - Fresh
          - Smoked
        - Powder

Soybean seeds are produced primarily for the production of oil and the protein in the meal. The average annual production in the United States,[5] 1936–45, was 109,519,000 bushels, of which 15.1 per cent was reserved for seed, 4.1 per cent fed to livestock on the farm where produced, and 73.3 per cent crushed. The last yielded 717 million pounds of crude soybean oil and 1,928,000 tons of cake and meal. The processing of soybeans is done in three ways, mechanical pressing, solvent extraction, and grinding undefatted bean, the last named process being used to produce full-fat flour or meal.

The marked increase in the production of soybeans in the United States has been paralleled by the development of numerous food, feed, and industrial uses for both the oil and the meal. The percentages of the annual factory consumption of soybean oil used for various purposes have been listed by Shollenberger and Goss[44] as follows: food industries (shortening, margarine, etc.) 70–93 per cent, drying oil industry (paint and varnish, linoleum and oilcloth, printing inks) 2–20 per cent, soap industry 1–6 per cent, and miscellaneous uses 1–5 per cent.

TABLE 23. PROPORTION AND COMPOSITION OF THE COMPONENT PARTS OF SOYBEAN SEED *

Component Part	Proportion of Seed %	Moisture %	Protein [Nx6.25] %	Carbo-hydrates %	Fat %	Ash %
Seed coat	8	12.53	7.00	21.02	0.60	3.83
Embryo:						
Cotyledons	90	10.57	41.33	14.60	20.75	4.38
Other organs	2	12.01	36.93	17.32	10.45	4.08

* Data from Bailey et al.[10]

The meal or cake remaining after processing for oil is highly nutritive and is used principally for livestock feeding. Minor quantities in the form of soy flours may be used to supplement wheat flour from a nutritional standpoint in the production of bread, other baked products, and in the form of flour and grits used as meat extenders. While these are the more important purposes for which the soybean and its products are used, the diversity of uses to which the different products of the soybean are put are shown in Table 22, prepared by Mr. W. J. Morse of the United States Department of Agriculture.

The average proximate composition of soybeans (Table 3) is characterized by being the highest in protein and ash contents, high in nitrogen-free extract and lowest in oil, compared with the other oil seeds. The soybean seed is made up of seed coat and embryo, the relative proportions and proximate composition of each as summarized by Bailey et al.[10] being given in Table 23.

That the composition of soybeans varies markedly as a result of differences in varieties, state of maturity, soil fertility, cultural and climatic conditions is attested by voluminous literature, typical of which are the investigations of Cartter and Hopper.[16] The degree to which the content of some of the constituents may be varied is illustrated in Table 24 by the maximum and minimum values reported by Bailey et al.[10] as a result of hundreds of analyses made by the United States Department of Agriculture.

Leading commercial varieties of soybeans usually contain from 18 to 21 per cent oil. While the oil from different lots of soybeans may vary considerably, commercial oils are relatively uniform. Soybean oil resembles quite closely cottonseed oil in both composition and properties (Tables 19 and 20). It is, however, somewhat higher in unsaturated and lower in saturated fatty acids, thus giving it a slightly higher iodine value. Materials other than glycerides of saturated and unsaturated fatty acids found in soybean oil include phosphatids, sterols, long-chain hydrocarbons, alcohols and ketones, free fatty acids, pigments, vitamins, antioxidants, and small amounts of mucilaginous substances.

TABLE 24. MAXIMUM, MINIMUM AND AVERAGE CHEMICAL COMPOSITION OF SOYBEANS *

Constituent	Minimum %	Maximum %	Average %
Moisture	5.02	9.42	8.0
Ash	3.30	6.35	4.6
Fat	13.50	24.20	18.0
Fiber	2.84	6.27	3.5
Protein	29.60	50.30	40.0
Pentosan	3.77	5.45	4.4
Sugars	5.65	9.46	7.0
Starch-like substances by diastase	4.65	8.97	5.6

* Taken from Bailey et al.[10]

The content and composition of soybean protein are important from a nutritive standpoint because of the extensive use of cake, meal, and flour as livestock feed and human food. Protein makes up a larger percentage of the soybean than any other of its constituents (30 to 50 per cent). Osborne and Campbell[42] concluded that a globulin which they named *glycinin* represented 80 to 90 per cent of the total crude protein; they also isolated a second globulin similar to phaseolin and an albumin-like proteid designated *legumelin*. The amino acid content of soybean meal (Table 5) is characterized by a relatively high content of the essential amino acid lysine, as well as being a good source of other essential amino acids.

The vitamin content of soybean meal (Table 8) is somewhat lower than that of other oil seeds in thiamine, riboflavin, and niacin. The meal is not considered a very good source of vitamins except thiamine. As compared with cottonseed (Table 6), soybeans are somewhat richer in calcium and potassium but poorer in iron than cottonseed.

Other Seeds

In addition to the oil seeds already discussed in detail, mention should be made of some of minor importance in the production of vegetable oils such as sesame, hemp, poppy, rape, castor, and safflower. Of these, sesame is the most important, producing an edible oil which serves as a substitute for olive oil. Hemp and rape produce semidrying oils, whereas poppyseed oil belongs to the drying class. Castor is a nondrying oil used chiefly as a purgative in medicine and, because of its high viscosity at high temperatures, as a lubricant for special purposes. Safflower is a drying oil, used in the manufacture of paints, varnishes, and linoleum. The properties and characteristics of these oils have been summarized by Jamieson.[25]

Table 25. Proximate Composition of Larger Seeded Legumes *

Food	Moisture %	Protein %	Fat %	Ash %	Fiber %	N-free Extract %
Common beans	10.5	22.0	1.5	3.9	3.9	58.2
Peas						
Whole	11.6	23.8	1.4	3.0	5.4	54.8
Split	10.0	24.5	1.0	2.8	1.2	60.5
Lentils						
Whole	11.2	24.7	1.0	3.2	3.3	56.6
Split	12.2	24.0	1.2	2.2	1.7	58.7

* Compiled from Chatfield and Adams.[17]

Of secondary importance in human nutrition compared with the cereals and oil seeds previously discussed, yet nevertheless of some significance in certain parts of the world, are some of the larger seeded legumes, especially the dry edible beans, peas, and lentils. They are prized not only for their high energy values but also for the highly important proteins which they supply to the diet. Thus they are particularly valuable in supplementing the cereals in areas where the population can make but limited use of the more expensive protein in animal products. Proximate composition data for these seeds are presented in Table 25.

BIBLIOGRAPHY

1. Alderks, O. H., *Chem. Ind. News* 23: 1168 (1945).
2. Alsberg, C. L., *Wheat Studies,* Food Research Inst. 15: 337 (1939).
3. Anderson, J. A., and Eva, W. J., *Board of Grain Commissioners for Canada Bull.* 4 (1943).

4. Andrews, J. S., Boyd, H. M., and Terry, D. E., *Cereal Chem.* **19**: 55 (1942).
5. Anonymous, Agricultural Statistics, 1946. U. S. Dept. Agr.
6. Anonymous, Census of the United States, Sixteenth: 1940, Manufacturers 1939, Vol. 11, Part 1. Reports by Industries Groups 1 to 10, Bur. Census, U. S. Dept. Commerce.
7. Anonymous, "Corn in Industry." New York, Corn Industries Research Foundation.
8. Anonymous, *U. S. Dept. Agr. Bur. Agr. and Ind. Chem. Mimeo. Circ. Ser.* **189** (1942).
9. Bailey, C. H., *Minnesota Agr. Expt. Sta. Tech. Bull.* **147** (1941).
10. Bailey, L. H., Capen, R. G., and Le Clerc, J. A., *Cereal Chem.* **12**: 441 (1935).
11. Barham, H. N., Wagoner, J. A., Campbell, C. L., and Harclerode, E. H., *Kansas Agr. Expt. Sta. Bull.* **61** (1946).
12. Baughman, W. F., and Jamieson, G. S., *J. Am. Chem. Soc.* **43**: 2696 (1921).
13. Beeson, K. C., *U. S. Dept. Agr. Misc. Publ.* No. **369** (1941).
14. Bidwell, G. L., Bopst, L. E., and Bolling, J. D., *U. S. Dept. Agr. Bull.* **1129** (1923).
15. Block, R. J., and Bolling, D., "The Amino Acid Composition of Proteins in Food." Springfield, Ill., Chas. C. Thomas (1945).
16. Cartter, J. L., and Hopper, T. H., *U. S. Dept. Agr. Tech. Bull.* **787** (1942).
17. Chatfield, C., and Adams, G., *U. S. Dept. Agr. Circ.* **549** (1940).
18. Coe, M. R., *U. S. Dept. Agr. Circ.* **190** (1931).
19. Earle, F. R., Curtis, J. J., and Hubbard, J. E., *Cereal Chem.* **23**: 504 (1946).
20. Ellis, N. R., and Madsen, L. L., *U. S. Dept. Agr. Bur. Animal Ind. A.H.D. Multigraphed Publ.* No. **61** (1943).
21. Fraps, G. S., *Texas Agr. Expt. Sta. Bull.* **191** (1916).
22. Geddes, W. F., "The Chemistry and Technology of Food and Food Products," M. B. Jacobs, editor. Vol. 2. New York, Interscience Publishers (1944).
23. Guthrie, J. D., Hoffpauir, C. L., Steiner, E. T., and Stansburg, M. F., *U. S. Dept. Agr. Bur. Agr. and Ind. Chem. Mimeographed Publ.* **AIC 61** (1944).
24. Hopkins, C. G., Smith, L. H., and East, E. M., *Illinois Agr. Expt. Sta. Bull.* **87** (1903).
25. Jamieson, G. S., "Vegetable Fats and Oils." New York, Reinhold Publ. Corp. (1943).
26. Johns, C. D., and Jones, D. B., *J. Biol. Chem.* **28**: 77 (1916).
27. Jones, D. B., *Cereal Chem.* **14**: 771 (1937).
28. Jones, D. B., and Csonka, F. A., *J. Biol. Chem.* **64**: 673 (1925).
29. Kik, M. C., *Cereal Chem.* **20**: 103 (1943).
30. Kik, M. C., *Rice* **46**: 14 (1943).
31. Kik, M. C., and van Landingham, F. B., *Cereal Chem.* **20**: 563 (1943).
32. Kik, M. C., and van Landingham, F. B., *Cereal Chem.* **21**: 154 (1944).
33. Kummerow, F. A., Barham, H. N., and King, H. H., *American Miller and Processor* **75**: 94 (1947).
34. Le Clerc, J. A., *Cereal Chem.* **10**: 383 (1933).
35. Le Clerc, J. A., and Wahl, R., *U. S. Dept. Agr. Bur. Chem. Bull.* **124** (1909).
36. McCance, R. A., Widdowson, E. M., Moran, T., Pringle, W. J. S., and Macrae, T. F., *Biochem. J.* **39**: 213 (1945).
37. Morrison, F. B., "Feeds and Feeding." Ithaca, New York, The Morrison Publ. Co., 20th ed. (1936).
38. Osborne, T. B., *Am. Chem. J.* **14**: 629 (1892).
39. Osborne, T. B., *J. Am. Chem. Soc.* **17**: 539 (1895).

40. Osborne, T. B., Carnegie Inst. of Wash., Washington, D. C., Publ. **84** (1907).
41. Osborne, T. B., "The Vegetable Proteins." New York, Longmans, Green (1912).
42. Osborne, T. B., and Campbell, G. F., *J. Am. Chem. Soc.* **20**: 419 (1898).
43. Sherwood, R. C., Nordgren, R., and Andrews, J. S., *Cereal Chem.* **18**: 811 (1941).
44. Shollenberger, J. H., and Goss, W. H., *U. S. Dept. Agr. Bur. Agr. and Ind. Chem. Mimeographed Publ.* **AIC** 74 (1945).
45. Smith, A. K., Johnson, V. L., and Beckel, A. C., *Ind. Eng. Chem.* **38**: 353 (1946).
46. Sullivan, B., and Bailey, C. H., *J. Am. Chem. Soc.* **58**: 383 (1936).
47. Thomas, J. M., Bina, A. F., and Brown, E. B., *Cereal Chem.* **19**: 173 (1942).
48. Vassel, B., *Arch. Biochem.* **11**: 405 (1946).
49. Vassel, B., and Nesbitt, L. L., *J. Biol. Chem.* **159**: 571 (1945).
50. Williams, V. R., Knox, W. C., and Fieger, E. A., *Cereal Chem.* **20**: 560 (1943).
51. Winton, A. L., and Winton, K. B., "The Structure and Composition of Foods." Vol. 1. New York, John Wiley and Sons (1932).

Chapter II

THE CHEMISTRY OF FRUIT AND VEGETABLE CROPS

Harry W. von Loesecke

Bureau of Agricultural and Industrial Chemistry, U. S. Department
of Agriculture, Washington, D. C.

Z. I. Kertesz

N. Y. State Agricultural Experiment Station, Cornell University,
Geneva, New York

During the past fifty years farm output in the United States has increased by more than two-thirds. This upsurge has been due to such factors as farm mechanization, new methods of insect and weed control, increasing interest in labor simplification and rearrangement of farm work, improved methods of drainage and irrigation, expanded use of soil conserving and soil-building practices, plant improvement, and the increased use of fertilizers.[2] Production will be further increased in years to come because of new tools of agricultural research; perhaps the most important of these new tools is the use of radioactive tracer elements.

Farming today has of necessity become a highly mechanized procedure. There is a vast gulf between the small farm of yesterday and the giant agricultural unit of today. As an example of modern vegetable production may be mentioned Seabrook Farms in southern New Jersey, claimed to be the world's largest. Here there are over 19,000 acres in crop cultivation, plus about 20,000 acres of contracting farms, employing about 5000 people at peak season and producing 75 million pounds of food annually. The vast farm is divided into eight operating units, each with its own planting schedules, labor force, machinery, and shops. Headquarters provides over-all direction and specialized functions of insecticide control, major maintenance, research, and personnel. Technicians and division managers keep contact with central supervision by means of a two-way radio system. Four planes, based at the farm's landing field, are used for spraying and dusting the crops. There is a full time soil conservation unit for building diversion and cropland terraces to ease the flow of eroding rainfall and melting snows.

Per capita consumption in the United States of fresh vegetables (exclusive of white and sweet potatoes and dry beans) has increased about 20 per cent during the past ten years. Per capita consumption of fresh fruits, with the exception of citrus, has shown a decrease during this same period; citrus consumption has increased over 65 per cent.

ORIGIN OF OUR FRUITS AND VEGETABLES

Few of the fruits and vegetables now consumed in the United States originated in this country. The *tomato* is a comparatively new crop, for the oldest records of it date back to less than 400 years.[34] It is of tropical origin and was early planted in the maize fields of the ancient Mexicans who called it *tomati*. Because the tomato is perishable and the Mexicans lacked knowledge as to its proper preservation, the vegetable never seemed to have attained an important place in the lives of these people. Prior to 1860 no tomato varieties had been developed in the United States.[8]

Peppers were probably introduced into Europe by Columbus who took specimens from the West Indies during his first voyage.

The *eggplant* was referred to in Chinese writings of some 1500 years ago, and by various writers in the 6th, 9th, 12th, and 13th centuries.[34]

Cucumbers are very likely native to India,[68] and records show that they were used in ancient Egypt and were popular with the Greeks and Romans.

The *muskmelon* was also probably native to India,[68] although there are indications that it was in use about the beginning of the Christian Era. Its cultivation spread to China and Japan but was never highly developed in those countries. It reached a high state of development in Iran (Persia), Turkistan, and about the Mediterranean. Columbus first brought species of the melon to the New World, and by 1535 it was being grown by the Indians as far north as Montreal, Canada.[70]

The *watermelon* is believed to be native of tropical Africa and was probably in cultivation for thousands of years, because it has been mentioned in ancient Sanskrit.

Pumpkins and *squash* are no doubt of American origin, although Vavilov[68] disputes this. It is stated that fragments of stems, seeds, and fruits were recovered from cliff dwellers ruins of the southwest United States[21] and some of the material was from the basket makers whose civilization antedates that of the cliff dwellers. In fact, the basket weavers are the oldest agricultural people of record in the United States.

Onions apparently date back to remote antiquity, and they were offered on the altars of the gods of Egyptian priests. Biblical history records that onions were one of the things longed for by the Israelites in the Wilderness.

The writings of the old Greeks and Romans contain mention of *peas;* and Columbus grew them on Isabella Island in 1493. Colonial Indian fighters found peas growing in western New York about 1779. Pickering[54] states that peas can be traced back even to the Stone Age.

Beans were introduced into Europe and Asia from the Americas, and European writings of around 1542 mention them. By 1616 a large number of varieties of different types were described.

The use of *cabbage* as a food antedates written history and has probably been in rather common use for more than 4000 years. Heading cabbage is described by Pliny.

Sweet potatoes originated in Mexico; and the *white potato* was found growing in South America by the Spanish invaders. *Turnips, rutabagas, beets,* and *parsnips* originated in Central and Western China, Middle Asia and Near Asia, and the Mediterranean.

Lettuce is a native of India and is one of the oldest of vegetable crops. It is mentioned in the writings of Herodotus, Pliny, Hippocrates, and Aristotle. It was reported in China as early as the 5th century A.D., and Chaucer mentions it in his writings of about 1340.

Corn was cultivated by the North American Indians, particularly by the Iroquois and the tribes of the upper Missouri. It was observed west of the Susquehanna by early Colonial Indian fighters.

The *strawberry* apparently came from North America, and its commercial development came about principally after the Civil War. In fact, most varieties now grown have originated within the past fifty years.

Blackberries, raspberries, and *blueberries* probably originated in North America where they have been cultivated from the wild varieties.

Apples were no doubt found by prehistoric man in roaming through the woods of western Asia and temperate Europe. The apple as we know it today has been greatly improved by the selection of best types of seedlings and then by budding and grafting. The apple was brought to the United States by the earliest settlers and rapidly disseminated from coast to coast.[46]

The history of the *pear* closely follows that of the apple. Nearly 1000 years before the Christian Era, Homer listed pears as one of the fruits in the garden of Alcinous. Theophrastus (370–286 B.C.) described grafting. The pear was distributed throughout temperate Europe by the migrating Romans.

Grapes are told of in ancient writings and ancient myths and fables. Grape seeds have been found in the remains of lake dwellings of the Bronze Age in Switzerland and Italy, and in ancient Egyptian tombs. The early American Colonists understood the culture of the vine along the Atlantic seaboard, and the Mission Fathers introduced the grape into California about 1769.

The *peach* probably originated in Persia, and was introduced into Greece shortly after the beginning of the Christian Era. It was long known in China and is mentioned in the writings of Confucius in the 5th Century B.C.

Plums originated in Europe, and pits were brought to North America by the first colonists and may have been planted by the Pilgrims in Massachusetts. The native American plum was used by the Indians long before the white man came.

Citrus fruits have been cultivated for thousands of years in the Orient and are native to southeastern Asia, eastern India, Indo-China, southern China, and the Philippines.[67] From the Orient various types spread to other parts of the world. Introduction of citrus into the Americas is a controversial subject among historians. The fruit was probably established at St. Augustine, Florida, in 1579, and in Peru before 1591. Franciscan monks at San Diego, California, introduced citrus into that region.

METHODS OF UTILIZING FRUITS AND VEGETABLES

Although fruits and vegetables are thought of as being primarily used for human food, yet in some instances they may be utilized as a raw material for industrial purposes, or for animal feed. Thus, commodities which because of size or color are not suitable for the fresh produce market, or because of incipient spoilage are not satisfactory for processing for human food, or because of glutted markets are uneconomical of shipment, may be diverted to other uses.

As examples: citrus fruits may be dried for cattle feed or even returned to the groves for fertilizer; carrots may be used for the extraction of carotene; leafy vegetables for the preparation of chlorophylls and carotenoid pigments; waste fruit for the manufacture of industrial alcohol, although the economics of such a venture is open to question.

A significant percentage of fruits and vegetables grown never reach the produce market, but are processed for food by canning, freezing, salting, drying, treated with sulfur dioxide or made into preserves (Table 26).

An outline of the more important methods of preservation is given in Table 27. Additional information will be found in the following paragraphs.

Canning involves heating the cleaned and properly prepared commodity at sufficiently high temperatures to inactivate enzymes and to destroy pathogenic organisms, yeasts, and molds. Fruits and their juices are generally heated at temperatures of from 190° to 212° F. for a specified period of time; but low-acid foods, such as vegetables, must be processed at higher temperatures: usually at 240° F. The product is protected from reinfection by sealing in cans or glass containers.[4, 15, 43, 6]

In the **freezing** of fruits and vegetables, the fresh product is prepared in essentially the same manner as for canning, and then subjected to temperatures as low as − 26° F. The product is usually packed into paraffined cartons with a moisture-vapor-proof inner liner, although metal containers may be used. Some commodities, such as peas, may be frozen in bulk and then packed into containers. Frozen foods are stored at 0° F., these low storage temperatures preventing bacterial spoilage.[26, 36, 67]

Dehydration implies the partial removal of water by artificial heat under carefully controlled conditions of temperature, humidity, and air-flow.[43]

TABLE 26. APPROXIMATE PERCENTAGES OF TOTAL 1945 PRODUCTION OF CERTAIN FRUITS SOLD AS FRESH PRODUCE AND UTILIZED FOR PROCESSING. (Calculated from Agricultural Statistics)

Commodity	Fresh Sales %	Canned %	Dried %	Frozen %	Farm Use %	Other Use %
Apples	70.0	5.4	8.6	3.6	4.3	8.1
Apricots	23.4	34.9	22.3	17.6	1.6	0.2
Cherries	33.4	32.1	16.5[1]	9.9	7.0	1.1
Cranberries	51.4	41.8	6.8			
Grapes	19.2	0.4	35.0		1.0	44.4
Grapefruit	44.4	55.6		–[2]	–[2]	–[2]
Oranges	73.6	26.4		–[2]	–[2]	–[2]
Peaches	56.4	24.1	7.8	2.9	8.5	0.3
Pears	58.6	29.1	3.8		8.2	0.3
Plums	91.3	3.0		1.4		4.3
Prunes	9.1	38.0	33.4	1.4	9.3	8.8

[1] Brined. [2] No data available.

Drying, on the other hand, implies the partial removal of water under conditions not so carefully controlled as in the case of dehydration. Most vegetables must be blanched in steam or hot water prior to dehydration to inactivate enzymes; in some instances sulfur dioxide is also used. Most fruits are exposed to fumes of burning sulfur prior to drying and may also be blanched before drying to prevent darkening and other deteriorative changes. The keeping quality of dehydrated foods is due to their low moisture content, presence of sulfur dioxide (where used) and concentration of sugars.[8a, 48, 50, 51]

Preservation by salting involves the addition of salt to the vegetable. Under proper conditions, a lactic acid fermentation takes place, and the acidity of the final product aids in its keeping. Sauerkraut and cucumber pickles are prepared in this manner.[22, 28, 39, 40]

Some fruits and their juices may be preserved with **sulfur dioxide,** or a salt of sulfurous acid.[19, 24, 71] This chemical suppresses the growth of yeast and mold. Foods preserved in this manner must be packed in wooden or glass containers. Tin containers will reduce sulfur dioxide to hydrogen sulfide with resulting offensive odors.

In some instances, processing plants are a part of the vegetable or fruit producing unit so that material not considered suitable for the fresh produce market can be immediately processed without loss of quality.

TABLE 27. METHODS OF PRESERVATION OF THE MORE IMPORTANT FRUITS AND VEGETABLES FOR COMMERCIAL PACKS (ORIGINAL) *

Method of Preservation	Commodity
Canning	**Fruits**
	Apple juice; apple sauce; baked apples; apricots; apricot nectar; blackberries; blueberries; cherries; cranberry sauce; fruit cocktail and salads; figs; grapefruit juice and sections; grapes; gooseberries; lemon juice; lime juice; orange juice; orange sections; orange and grapefruit juice; orange concentrate; peaches; pears; plums and prunes; loganberries; raspberries; pineapple juice and slices; strawberries; tangerine juice.
	Vegetables
	Asparagus; string beans; lima beans; baked and processed beans; beets; carrots; peas and carrots; celery; corn; hominy; olives; peas; pimiento; okra; spinach; sweet and white potatoes; tomatoes; tomato juice and puree; rhubarb; pumpkin; squash.
Freezing	**Fruits**
	Apples; apple sauce; blueberries; apricots; cherries; currants; gooseberries; grapefruit sections; fruit salads; Boysenberries; orange juice and concentrate; lemon juice; nectarines; peaches; pineapples; plums and prunes; raspberries; loganberries; strawberries.
	Vegetables
	Asparagus; string beans; lima beans; broccoli; baked beans; Brussel sprouts; carrots; cauliflower; corn; peas; spinach; rhubarb; succotash; pumpkin; squash; Swiss chard.
Dehydration and Drying	**Fruits**
	Apricots; apples; bananas; cranberries; figs; grapes; nectarines; peaches; pears; prunes.
	Vegetables
	Cabbage; sweet and white potatoes; carrots; rutabagas; beets; onions; garlic; parsley; peas; beans; spinach; corn; lima beans; peppers; celery tops; tomato juice.
Salting	Cabbage; cauliflower; onions; peppers; cucumbers; olives.
Sulfur dioxide	Lime juice; grapefruit juice; orange juice; cherries; strawberries; peaches.

Note: Fruits and vegetables not mentioned may be packed commercially in small amounts.

IMPORTANCE OF WATER AS A PLANT CONSTITUENT

As a rule plant physiologists fully appreciate the importance of water in fruits and vegetables, but chemists concentrate their attention on the other constituents, usually lumped under the designation ''total solids.'' True enough, the water in fruits and vegetables is of little significance from the standpoint of nutrition. But water plays a dominant part in growing and maturing plants in determining yields as well as in the quality and commercial value of the product. The availability of water will also influence the chemical composition of the commodity. For instance, tomatoes grown with a restricted supply of water will contain more acid than those from plants with an abundant water supply.[41]

The discussion of the role of water in the growing of fruits and vegetables is outside the scope of this chapter (see Chapter VII, Volume I), yet a few remarks relative to water always present in plant tissue might be desirable. Fruits and vegetables show a wide range of water content from a very low proportion as in mature seeds of legumes, cereals, and in nuts, to over 90 per cent as, for instance, in tomatoes and watermelons. More important than the water content is the influence of water on the physical appearance and behavior of almost any fruit and vegetable. The firmness and crispness of such tissues depend to a great extent on the turgor pressure which forces the cytoplasm tightly against the cell wall. Any disturbance of the natural water balance in the tissue might upset conditions, and wilting and other undesirable reactions may result. Unfortunately, the factors governing the water balance in plant tissues are not completely understood [17] but it is clear that both osmotic pressure and the forces of imbibition exhibited by colloids have an important role.

The water in various types of plant tissues seems to be held by different types of affinities. Some water at times is held in a manner to become designated as "bound water" [27] and may be distinguished from the rest of the water present in the tissue by differences in behavior. Such bound water is assumed to play an important role in the resistance of plants to freezing and also in the dehydration of fruits and vegetables. In spite of the great importance of water in plants, little is known about the exact form or forms in which it exists in the tissues. This problem is intimately related to the changing conception of colloid chemistry.

It is known that water participates in many reactions which occur in plant tissues. When polysaccharides are formed from the simpler sugars, a molecule of water is released as two molecules combine. Conversely, water is introduced into polysaccharides as starch, pectins, or sucrose as these are hydrolyzed into their monomeric components. Since one might regard a living plant tissue as representing a complex of many syntheses and hydrolyses progressing in an organized manner, the important role of water will be obvious. When growing peas suffer from lack of water, more polysaccharides like starch and dextrins are formed than with an adequate water supply.[38]

It should be noted that the exact water content of a plant tissue is a debatable matter since any numerical value will depend on the method with which the results are obtained. Sometimes plant material is dried at 100° C., while in other cases lower temperatures and a partial vacuum are used. Endless variations of the three factors such as temperature, pressure, and length of treatment can be found in the methods described in the literature. In light of what has been said above, it is noteworthy that the evaporation of water from a fruit or vegetable is quite rapid until the water content is reduced to a value characteristic to the tissue and in the neighborhood of 10 to 15 per cent. Thereafter evaporation is slow. In recent years extensive use has been made of the titrimetric determination of water content of plant tissues.[57] This shows promise of being more scientifically correct than determinations made with the application of heat.

SOME FACTORS AFFECTING THE COMPOSITION OF FRUITS AND VEGETABLES

Fruits and vegetables may vary widely in composition because of a number of factors. Of chief importance are climatic conditions, fertilizer and cultural practices, soil characteristics, irrigation, time and method of harvest, and variety and strain.

TABLE 28. PERCENTAGE COMPOSITION OF CORN OF DIFFERENT TYPES AND VARIETIES AT 30 DAYS STAGE OF MATURITY *

Variety	Total Solids %	Total Sugar %	Reducing Sugars %	Polysaccharides Sucrose %	Polysaccharides Total %	Polysaccharides Water Soluble %
Mandan White [flour]	52.40	1.25	0.15	1.10	37.43	1.86
Yellow Assiniboine [flour]	48.75	1.35	0.12	1.23	35.06	1.38
Waxy Maize	55.76	1.80	0.24	1.56	40.39	5.47
Rhode Island White [flint]	51.00	2.24	0.37	1.87	35.14	2.86
Longfellow [flint]	54.02	1.79	0.17	1.62	37.31	2.56
2nd Early Adams [dent]	42.52	1.86	0.23	1.63	29.07	1.82
Stowell's Evergreen [sweet]	32.18	2.78	0.63	2.15	20.89	12.18
Golden Bantam [sweet]	41.27	1.31	0.37	0.94	27.43	12.67

* Condensed from Culpepper, C. W., and Magoon, C. A., *J. Agr. Res.* **34**: 413–433 (1927).

Agricultural chemists have accomplished a tremendous amount of research in this field, and much remains to be done. The extensive literature dealing with the results of this work can be covered only briefly in the present chapter. Discussion will be confined to pointing out some of the more illustrative cases.

Difference in Composition Due to Variety. Data on the composition of different fruits and vegetables may be misleading unless the variety (and possibly region of production) is stated, because in general the composition will vary with variety and, in many instances, with region of growth. The former variation is illustrated in Tables 28 and 29. In the case of oranges, composition of the juice will even vary with the rootstock and size of the fruit: juice from small fruit will contain more acid and more total soluble solids than the juice from larger sizes.[35]

Variation in Composition Due to Fertilizer Practices and Soil Characteristics. In a recent study Wittwer[72] found that application of nitrogen to New Zealand spinach increased the yield of vegetation which generally became progressively inferior in nutritional value with each increment of nitrogen. On the other hand, Ellis and Hamner[20] and Hamner et al.[31] have indicated that so far as ascorbic acid content is concerned, the tomato fruit is little influenced by the supply of mineral nutrients to the plant. With a leafy vegetable, such as turnip greens, the researches of Bernstein et al.[6] showed no appreciable effect of fertilizer treatment on the carotene content of plants grown in soil, but in sand cultures, deficiencies of sulfur, nitrogen, and potassium caused a decrease in carotene, while a deficiency of phosphorus resulted in no decrease. Reder et al.[55] experimenting along the same line found that results varied with different localities.

TABLE 29. CAROTENE CONTENT OF DIFFERENT VARIETIES OF CARROTS *

Variety	Carotene Content [mg./100 g. dry wt.]		
	7/1/42	8/1/42	9/1/42
Imperator	44	79	80
Danvers Half Long	56	72	74
Chantenay	87	--	96
Morse Bunching	56	62	80

* Von Loesecke, Harry W., "Drying and Dehydration of Foods." Reinhold Publishing Corporation, New York, page 99, 1943.

From the above it will be seen that not all fruits and vegetables will respond to fertilizer practices by a change in composition. The reason for this is not clearly understood, but it is quite probable that the environmental factor is of greater importance than that of fertilization. Another reason for lack of response, particularly where there is failure to increase vitamin content, may be due to the fact that plants lacking proper nourishment contain a lesser quantity of vitamins because of a deficiency in metabolism. As soon as the nutritional requirements of the plant are met by the addition of sufficient nourishment, the metabolism of the plant proceeds in a normal manner and the vitamin content is raised to an optimum height. Further fertilization will not increase the vitamin content above this optimum value. The chance of increasing the vitamin content through the addition of fertilizers is therefore based solely on raising a too-low vitamin quantity of a poorly nourished plant to the "normal" average index.[25]

MacGregor and Rost,[45] working with Red River Valley potatoes, found that application of muriate of potash greatly increased the chlorine concentration in the potato tissues. Leichsenring and co-workers[42] reported that application of superphosphate at the rate of 200 pounds per acre in Minnesota areas produced an increase in reduced and total ascorbic acid in potatoes, while muriate of potash at the rate of 100 pounds per acre tended to decrease reduced and total ascorbic acid when results were expressed on a wet basis. There was no change if results were expressed on a dry basis.

In the case of bananas, it has been found[63] that chloride and sodium showed definite correlation between soil composition and the composition of the ash of the pulp of the fruit.

As another example, citrus grown in the heavy muck soils of the northern fringes of the Florida Everglades have characteristics different from those of fruit grown in the sandy soils of the ridge section of Florida.

Influence of Climatic Conditions. Perhaps of even greater influence than fertilizer practices on the composition of fruits and vegetables is that of environment. Reder et al.[55] obtained wide variations in the ascorbic acid content of turnip greens produced in different localities. Those produced, for example at Norfolk, Va., contained a mean value of 2.41 mg./g. of ascorbic acid; while those grown at Blacksburg, Va., contained a mean value of but 1.28 mg./g.

Smith et al.,[60] working with oranges in the Salt River Valley of Arizona, found that fruit on the south side of the trees had significantly more ascorbic acid than fruit from the other sides of the tree. Harding[32] reported similar results from Florida in that oranges from outside branches which were exposed to the sun contained more ascorbic acid than shaded fruit.

Saywell and Cruess[56] found that the average total solids and sugar content of tomatoes of a given variety grown in the cool, foggy climate of the San Francisco Bay region of California were higher than those of the same variety grown in the hot and dry Sacramento Valley. It would also appear that California grown tomatoes are higher in total solids than those grown in the eastern United States, although the data are not perhaps sufficiently extensive to warrant definite conclusions.

Leichsenring et al.[42] in their researches on potatoes in Minnesota areas found environmental factors to be apparently of greater importance than fertilizer practice on the ascorbic acid content of the tubers.

The effect of climatic conditions on the composition of apples has been rather extensively studied by Shaw[58] and by Caldwell.[10, 11]

Influence of Cultural Practices. Cultural practices in some instances are influential in affecting the composition of fruits and vegetables. Such practices would include, for example, irrigation, spraying, and methods of cultivation. If the latter should result in mutilation of the growing plant, certain well-defined changes may be expected. Thus, Culpepper and Magoon [16] found that mutilation of corn plants (such as defoliation or root pruning) influenced the yields, size of ears, number of kernels, and even the chemical composition of the grains. The extent of these changes depended upon the stage of maturity of the plant when mutilation took place.

Arsenic is known to affect profoundly the composition of oranges, grapefruit, and tangerines if the trees are treated with sprays containing an arsenic salt.[30, 33] The most significant effect is a reduction in total acidity. A decrease in ascorbic acid may also result, if arsenic concentrations are sufficiently high. The extent of the effects brought about by arsenic sprays depends upon the time of spraying, type of fruit, age of trees, and concentration of arsenic in the spray. Phosphoric acid will give practically the same results as arsenic.[64]

Change of Composition with Maturity. As fruits and vegetables mature, there are well-marked changes in chemical composition. Thus, as corn ripens sugars decrease and starch increases. In the case of apples there is an increase in sugars and a decrease in starch. Oranges, grapefruit, and tangerines show an increase in total solids and sugars and a decrease in acidity; lemons, on the other hand, increase in acidity during ripening.

Ripening of tomatoes is indicated by a decrease in total solids, and an increase in acidity and generally an increase in total pectin.

Bananas, with the exception of the Plantain, showed a marked increase in total sugars and a decrease in starch.

PROXIMATE COMPOSITION OF SOME FRUITS AND VEGETABLES

The term "proximate" is commonly used for an analysis that is approximate and not complete in every detail.

The importance of definite knowledge of the chemical composition of foods has long been recognized, and the exact determination of such chemical values has had a gradual and steady growth over a period of years. Perhaps the first analysis of American foods was made over one hundred years ago when the mineral constituents of rice, rice straw, and chaff were determined.[59] Subsequent years brought forth other studies in composition culminating in 1896 in the publication of Atwater and Bryant's [5] extensive compilation of the proximate composition of American food materials, a piece of work that has been a standard reference since its publication. Over a period of years, Atwater and Bryant's tables have been recalculated, modified, and data have been added to take into consideration the development of new varieties of fruits and vegetables and new cultural methods.[13, 14]

Food composition tables generally contain values for moisture, protein, fat, crude fiber, carbohydrates, nitrogen-free extract, and sometimes acid. The meaning of these terms is described briefly below:

Protein is calculated by multiplying the nitrogen content by a factor, usually 6.25. This factor is not strictly correct in every instance because it is based on two assumptions: (1) that all proteins contain 16 per cent nitrogen, and (2) that all nitrogen in a food is in the form of protein. These are both incorrect, since all proteins do not contain the same percentage of nitrogen, and because all foods contain some nonprotein nitrogen. In some foods, such as tubers, roots, leafy vegetables, and yeast, nonprotein nitrogen may be considerable. Because of the misuse of the factor 6.25, the protein values in many tables of food composition are approximations, although in most instances the error is small.

Recent data supplied by the Food and Agriculture Organization of the United Nations has indicated that the factor 6.25 may be applied to nitrogen in foods, other than those specified below without serious error.

Cereal Grains	*Factor Suggested*
Wheat flour, refined	5.70
Wheat, whole kernel	5.83
Rye, barley, oats	5.83
Rice	5.95
Oilseeds and Nuts	
Almonds	5.18
Brazil nuts	5.46
Peanuts	5.46
Soybeans	5.71
Others	5.30
Milk	6.38
Gelatin	5.55

Fat is generally determined by extracting the properly ground and dried sample with a fat solvent. This solvent is generally ethyl ether, and fat in some cases may be expressed as "ether extract." This method determines crude fats because the extract includes neutral fats, phospholipids and other substances in small amounts. A refinement in the method involves saponification which gives more specifically an estimate of the fatty acids alone. The extraction method is, however, more convenient.

Carbohydrates. "Total" carbohydrates in the majority of cases is calculated by difference, i.e., the difference between 100 per cent and the sum of the percentages of water, protein, fat, and ash. This method tends to overestimate the available carbohydrates because it also includes crude fiber and organic acids, when these are present, as well as any undetermined material. Some of the more recent determinations differentiate between starches, dextrins, sugars, and those polysaccharides whose availability for nutritive purposes is still doubtful. The ultimate purpose is of course to determine the fraction of a food material which is true carbohydrate that can be utilized by the human organism.

TABLE 30. PROXIMATE COMPOSITION OF EDIBLE PORTION OF CERTAIN SELECTED FRESH VEGETABLES *

Vegetable	Water %	Protein %	Fat %	Ash %	Total Carbohydrates %	Fiber %	Sugar %	Starch %
Artichokes	83.7	2.9	0.4	1.1	11.9	3.2	---	---
Asparagus, shoots	93.0	2.2	0.2	0.67	3.9	0.7	1.3	0.4
Beans, lima [shelled]	66.5	7.5	0.8	1.71	23.5	1.5	---	---
Beans, snap	88.9	2.4	0.2	0.77	7.7	1.4	0.4	2.2
Beets, com.red	87.6	1.6	0.1	1.11	9.6	0.9	---	---
Beet greens	90.4	2.0	0.3	1.7	5.6	1.4	0.5	---
Broccoli	89.9	3.3	0.2	1.1	5.5	1.3	1.9	---
Brussels sprouts	84.9	4.4	0.5	1.28	8.9	1.3	---	---
Cabbage	92.4	1.4	0.2	0.75	5.3	1.0	3.5	---
Cabbage, Chinese	95.2	1.4	0.1	0.89	2.4	0.6	0.9	0.2
Carrots	88.2	1.2	0.3	1.02	9.3	1.1	7.5	---
Cauliflower	91.7	2.4	0.2	0.85	4.9	0.9	2.6	---
Celery	93.7	1.3	0.2	1.08	3.7	0.7	1.2	---
Chard [leaves and stalk]	91.8	1.4	0.2	2.2	4.4	0.9	---	---
Chicory ["French endive"]	94.2	1.6	0.3	1.0	2.9	0.8	0.2	---
Chives	86.0	3.8	0.6	1.8	7.8	2.0	---	---
Collards	86.6	3.9	0.6	1.70	7.2	1.2	1.2	0.2
Corn, sweet	73.9	3.7	1.2	0.66	20.5	0.8	4.3	14.6
Cress, water	93.6	1.7	0.3	1.09	3.3	0.5	---	---
Cucumbers	96.1	0.7	0.1	0.44	2.7	0.5	2.6	---
Dandelion greens	85.8	2.7	0.7	2.0	8.8	1.8	0.7	0.2
Eggplants	92.7	1.1	0.2	0.54	5.5	0.9	---	---
Endives	93.3	1.6	0.2	0.89	4.0	0.8	----	---
Kohlrabi	90.1	2.1	0.1	1.05	6.7	1.1	2.2	---
Leeks	88.2	2.5	0.4	1.03	7.9	1.3	2.6	1.4
Lettuce	94.8	1.2	0.2	0.91	2.9	0.6	1.6	---
Mushrooms	91.1	[0]	0.3	1.14	[0]	0.9	---	---
Okra	89.8	1.8	0.2	0.84	7.4	1.0	---	---
Onions	87.5	1.4	0.2	0.58	10.3	0.8	6.7	0.5
Parsnips	78.6	1.5	0.5	1.15	18.2	2.2	9.5	2.4
Peas, shelled	74.3	6.7	0.4	0.92	17.7	2.2	3.2	8.2
Potatoes	77.8	2.0	0.1	0.99	19.1	0.4	0.9	14.7
Pumpkin, mature	90.5	1.2	0.2	0.82	7.3	1.3	2.5	2.6
Radishes	93.6	1.2	0.1	0.95	4.2	0.7	3.4	---
Rutabagas	89.1	1.1	0.1	0.83	8.9	1.3	6.7	---
Soybeans [shelled]	67.0	12.5	6.5	1.5		1.5	3.0	1.5
Spinach	92.7	2.3	0.3	1.53	3.2	0.6	0.3	---
Squash, summer	95.0	0.6	0.1	0.44	3.9	0.5	1.0	0.2
Squash, winter	88.6	1.5	0.3	0.83	8.8	1.4	3.9	1.0
Sweetpotatoes	68.5	1.8	0.7	1.07	27.9	1.0	5.4	20.2
Tomatoes, red	94.1	1.0	0.3	0.57	4.0	0.6	3.4	---[1]
Turnips	90.9	1.1	0.2	0.73	7.1	1.1	4.6	---
Turnip tops	89.5	2.9	0.4	1.76	5.4	1.2	---	---
Yams, winged	72.6	2.1	0.2	0.98	24.1	0.8	1.0	17.7

* From Chatfield, Charlotte, and Adams, Georgian. *U. S. Dept. Agr. Circ.* **549** (1940).

[1] 0.51% acid as citric.

There are at present few laboratories equipped to determine the separate components of the fraction "carbohydrate by difference." For this reason a great many tables of food composition do not attempt a separation of the components of this fraction and merely report "carbohydrate by difference."

Crude fiber is "the sum of all organic components of the plant cell membrane and supporting structure which in chemical analysis of plant foodstuffs remain after removal of crude protein, crude fat, and nitrogen-free extractives."[47] It represents the indigestible residue from plant foods; it does not occur in foods of animal origin. Crude fiber is determined by treating a sample of the dried, fat-free food with dilute sulfuric acid and then with dilute sodium hydroxide under certain specified conditions. Chemically, crude fiber is the cellulosic constituents of the food; as such it includes celluloses, hemicelluloses, and lignins.

TABLE 31. PROXIMATE COMPOSITION OF THE EDIBLE PORTION OF CERTAIN SELECTED FRESH FRUITS *

Fruit	Water %	Protein %	Fat %	Ash %	Total carbohydrates %	Fiber %	Sugars %	Acid %
Apples [all varieties]	84.1	0.3	0.4	0.29	14.9	1.0	11.1	0.47 [1]
Apricots	85.4	1.0	0.1	0.59	12.9	0.6	10.4	1.19 [1]
Bananas	74.8	1.2	0.2	0.84	23.0	0.6	19.2	0.39 [1]
Blackberries	85.3	1.2	1.1	0.47	11.9	4.1	6.1	0.91 [2]
Blueberries	83.4	0.6	0.6	0.28	15.1	1.2	9.7	0.67 [2]
Cherries, sour	84.4	1.3	0.5	0.51	13.3	---	9.5	1.38 [1]
Cherries, sweet	80.0	1.1	0.5	0.6	17.8	0.4	11.6	0.68 [1]
Cranberries	87.4	0.4	0.7	0.20	11.3	1.4	4.2	2.36 [2]
Currants	84.7	1.6	0.4	0.61	12.7	3.2	5.7	2.30 [2]
Gooseberries	88.3	0.8	0.4	0.39	10.1	2.5	0.4	2.32 [2]
Grapefruit	88.8	0.5	0.2	0.42	10.1	0.3	6.5	---
Grapes, American	81.9	1.4	1.4	0.45	14.9	0.5	11.5	1.21 [1]
Grapes, European	81.6	0.8	0.4	0.46	16.7	0.5	14.9	0.47 [1]
Lemons	89.3	0.9	0.6	0.54	8.7	0.9	2.2	5.07 [2]
Limes	86.0	0.8	0.1	0.8	12.3	--	0.5	5.9 [2]
Muskmellons	92.7	0.6	0.2	0.6	5.9	0.5	5.4	----
Oranges	87.2	0.9	0.2	0.47	11.2	0.6	8.8	0.68 [2]
Peaches	86.9	0.5	0.1	0.47	12.0	0.6	8.8	0.64 [1]
Pears	82.7	0.7	0.4	0.39	15.8	1.4	8.9	0.29 [2]
Pineapples	85.3	0.4	0.2	0.42	13.7	0.4	11.9	0.72 [2]
Plums	85.7	0.7	0.2	0.51	12.9	0.5	8.3	1.60 [1]
Raspberries, red	83.4	1.1	0.6	0.47	14.4	2.8	7.2	1.34 [2]
Raspberries, black	80.7	1.5	1.6	0.65	15.6	3.5	7.9	1.16 [2]
Rhubarb	94.9	0.5	0.1	0.72	3.8	0.7	0.4	----
Strawberries	90.0	0.8	0.6	0.50	8.1	1.2	5.3	1.09 [2]
Tangerines	89.2	0.9	0.3	0.4	9.2	---	7.8	0.83 [2]
Watermelons	92.1	0.5	0.2	0.27	6.9	0.6	6.0	0.03 [1]

* Chatfield, Charlotte, and Adams, Georgian. *U. S. Dept. Agr. Circ.* **549** (1940).

[1] As malic acid.

[2] As citric acid.

Ash represents the amount of mineral matter and is the material left after the organic portion has been burned away. From the standpoint of nutrition, total ash values are of little importance. Of greater significance to the nutritionist are the constituents of the ash, and particularly calcium, phosphorus, and iron.

Nitrogen-free extract is total carbohydrate excluding fiber. This measure is preferred by some workers for estimating the quantity of carbohydrates. It is the difference between 100 per cent and the sum of the percentages of water, protein, fat, ash and crude fiber.

Limitations in the Usefulness of Proximate Analyses. Tables of analyses of food composition are limited in their usefulness. The data, for example, may represent the analysis of only one sample of a given food. Again they may represent the mean of many samples which differ by reason of variety, climatic conditions under which they were grown, season, maturity, or change brought about by storage. Unless it is known to what extent these differences are significant, the data lose much of their value.

Since foods are not constant in composition, it is sometimes customary to report maximum and minimum values, as well as the average. Maximum and minimum values do not necessarily represent actual limits of variation which can occur, but merely indicate the range of composition of the particular samples analyzed. Typical proximate analyses are given in Tables 30 and 31.

Changes in Chemical Composition of Fruits and Vegetables During Harvesting, Storage, and Processing

When fruits and vegetables have reached their optimum maturity they are harvested for the fresh produce market, or for storage or processing. However, optimum maturity for processing is not necessarily the same as for storage or the fresh market. Well-marked changes in chemical composition of such commodities may occur during such operations, these changes varying with the degree of care with which the product is handled.

Changes which May Occur After Harvesting. Unrefrigerated harvested vegetables rapidly lose flavor and sweetness, and this is especially true of asparagus, sweet corn, peas, and lima beans. This is due to the fact that vegetables (and fruit) continue to respire after harvest, the respiration process using up sugar. Respiration is more rapid at high temperatures than at low temperatures, and sweet corn, for example, will lose 2.8 times more sugar when held for 96 hours at 86° F. than when held for the same period at 32° F. Peas will lose about 30 per cent of their sugar if held for six hours at 77° F. after harvesting. Spinach will also lose sugar if held at temperatures of between 60 and 70° F.

Peas and lima beans are commercially machine podded prior to canning or freezing, and are generally badly bruised during the threshing

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process. Bruising accelerates deterioration, because abnormal respiration is brought about which produces off-flavors. The bruised surfaces also will allow entrance for various microorganisms which will rapidly multiply under warm, favorable conditions and add to the deterioration in flavor and freshness.

Deteriorative changes in fruits are generally more evident to the eye than in the case of vegetables. If the skin of most varieties of peaches, apples, and pears is removed, permitting exposure of the pulp beneath, darkening will quickly occur. This is largely due to the enzymic oxidation of catechol-tannins which these fruits contain.

Strawberries will rapidly deteriorate in flavor after capping, probably because of loss of volatile flavor, and increased respiration brought about by trauma of the tissues during capping.

Bananas are always harvested while still green, but they will rapidly ripen if maintained at warm temperatures, and particularly if they are so confined as to permit them to be exposed to the products of their own respiration or to those of other fruits.

Citrus fruits quite often show shrinkage indicated by a loss in weight. Loss of weight tends to be greater in the smaller sizes than in the larger sizes probably because of the comparatively larger surface area of the former.

Changes which May Occur During Storage. The period of time during which fresh fruits and vegetables can be held in storage will depend upon variety, condition when harvested, region of growth, as well as other factors not as yet fully understood. There may be great variations in optimum storage temperatures and relative humidities between different fruits and vegetables.

Since fresh fruits and vegetables are alive, they carry on within themselves many of the vital processes characteristic of all living things. Cold storage (i.e., temperatures of approximately 30° to 45° F.) are used for the purpose of retarding these life processes. Thus, potatoes at 40° F. will evolve from 1100 to 1760 B.t.u. per ton per 24 hours, while at 70° F. they will evolve from 2200 to 3520 B.t.u. per ton per 24 hours. Apples at 32° F. will liberate from 660 to 880 B.t.u. per ton per 24 hours; at 85° F. this increased to from 6600 to 15400 B.t.u. per ton per 24 hours.

During storage, fresh fruits and vegetables will give off moisture, one of the products of respiration, and unless the surrounding atmosphere has a high relative humidity, the products will in time become shriveled or wilted, even though the temperature is as low as 32° F.

Enzymes contained in the fruits and vegetables will act upon various substances in the plant tissues and gradually bring about changes in color, texture and chemical composition, eventually resulting in serious deterioration or actual break-down.

Besides the chemical changes that occur because of respiratory activity, changes may be brought about by certain physiological or pathological disorders, such for example as water core of apples, low-temperature breakdown of cranberries, stem-end rot of oranges, membranosis of lemons, gray mold rot of pears and strawberries, soft rot of asparagus, slimy rot of cabbage, and slimy bacterial decay of lettuce.

Changes that May Occur During Processing. Before vegetables are frozen or canned they must be blanched. This involves heating in steam or hot water, and the chief purpose is to inactivate enzymes and fix the color. Blanching may leach out some of the salts, water-soluble vitamins, sugars, and proteins, destroy part of the ascorbic acid and flavor, and in the case of some vegetables, change a portion of the chlorophylls to pheophytin. Leaching is more serious in hot water blanching than in steam blanching. As much as 25 per cent of the sugars in peas may be leached out in water blanching. Loss is considerably less in steam blanching.

Fruits are not blanched, but changes may occur because of enzyme activity, as already pointed out, and result in discoloration. Changes in flavor may take place after the juice is extracted from certain fruits. Thus, orange juice after extraction rapidly changes in flavor, often becoming bitter. The exact cause of this has been the subject of considerable controversy among research workers.

Canning of fruits and vegetables may bring about further changes in composition. Chlorophylls in peas and spinach may be changed to pheophytin giving the product a dull, green appearance; there may be a loss of vitamins, and marked flavor changes generally occur. The reason for these flavor changes is little understood, but probably result from a loss of volatile constituents, or even to a chemical reaction between the constituents caused by high processing temperatures and possibly accompanied by oxidation.

In some instances there may be pronounced darkening or "browning" of the canned product. This may be due, at least in part, to a reaction between amino acids and sugars, or even organic acids and sugars. The mechanism of the browning reaction is still the subject of considerable research.

In the preservation of foods by freezing, many changes take place. Tressler and Evers[67] classify these changes into the following types: (1) physical, (2) chemical, (3) physicochemical. The first includes crystallization, expansion, and desiccation; the second ordinary chemical reactions caused by enzymes and by bacteria, yeasts, and molds.

There are profound changes in the colloidal condition of many frozen foods, the mechanism of which is not as yet well understood. Woodroof[73] in his studies of the changes taking place in fruit cells during freezing pointed out, among other things, that freezing destroyed the colloidal complex of the cells and reduced turgidity. This colloidal state was so completely destroyed it seemed doubtful if active absorption occurred.

Quality Factors as Affected by Chemical Constituents

The commercial value of fruits and vegetables is greatly influenced by their quality. The importance of quality is accentuated by abundant supplies and high purchasing power.

Generally speaking, the quality of any fruit and vegetable might be defined by appearance and color; texture or consistency, and flavor. Nutritional value is now also often included as a quality factor. In preserved or manufactured products, the processor is largely responsible for the quality of his products; in addition to using high quality raw material he must be successful in retaining the desirable characteristics of the raw product as well as observing good workmanship in other respects. It might be of interest to discuss in a general and concise manner some of the relations existing between quality and chemical composition of fruits and vegetables and also to point out the areas where the greatest lack of knowledge exists.

Appearance and Color. The appearance and color of a fruit or vegetable will depend mostly on the types of pigments present and the physical characteristics of the surface. In addition, various coatings as the wax on apples or the "bloom" on plums may definitely add or detract appeal.

During the past forty years a great deal of chemical knowledge has been acquired concerning the chemistry of plant pigments.[49] These are discussed in detail in Chapters IX and X in Volume I. The most important groups of these are the chlorophylls, the anthocyanins, the carotenoids, and the flavones. The *chlorophylls*[62] give plants their green color which will depend almost as much on the condition of the pigment in the tissue as on its quantity. While the chemical constitution of various chlorophylls is now fairly clear, little is known about the chemical reactions involved in their formation. Similarly, the reactions leading to the loss of chlorophyll are little understood. The chlorophylls are difficult to purify, but they can be quite easily identified by their unique absorption spectra. They are sensitive to heat and therefore some chlorophyll is usually lost in the canning of vegetables as pointed out above. A process has been developed to retain more color in the canning of peas[63] through chemical treatments to retain the chlorophyll color.

The *anthocyanins*[7] lend fruits and some vegetables their red, purple, and blue colors. The chemistry of this group of pigments is fairly well known. In spite of the great variations in the color intensities and hues found, they mostly possess the same basic structure with only slight variations in the positions and numbers of attached hydroxyl, methoxyl, and glycosidic sugar groups. Nothing positive is known about their formation. Grapes seem to contain different anthocyanins depending on the variety and other factors.[1] while the red anthocyanin of all or most cultivated strawberries seems to be the same pigment which is present in different quantities.[52] The anthocyanins show an undesirable degree of instability leading to a rapid loss of color in many products as for instance strawberry juice and preserves.[61] The reactions leading to the loss of color are not known.

The *carotenoids* [29] are yellow, orange, or red in color and include beta-carotene and its stereoisomers, and also lycopene, the dominant red pigment of tomatoes. Below 85° F. more lycopene than carotene is formed in tomatoes, while above this temperature the relationship is reversed. Carotenoids are susceptible to a number of different types of destruction. Beta-carotene is provitamin A and has an important nutritional function.

The *flavones* [49, 6a] are less intensely colored than pigments in either of the above groups. Their color ranges from white through yellow to orange. Certain "flavonoids" * as the rutin found in asparagus, buckwheat and over 38 other species of common plants, are important on account of their physiological action.

Color is a factor in most grade and quality evaluation schemes for fruits and vegetables and processed products from them. It is still customary to measure the color by comparison, although objective measurements have come to the fore during the past few years. Most of these latter are made in extracts which discount the possible effects of surfaces. Instruments for the measurement of the reflected color on the original fruit or vegetable itself are only now in the process of development.

The chemistry of the waxy coating [48] is complicated and the chemical nature of the coatings of only a few fruits and vegetables is known. In the case of apples, the waxy coatings differ among varieties both in quantity and composition.[48]

Texture and Consistency. Obviously the morphological structure of the tissue will have an important role in determining the texture and consistency of fruits and vegetables. The fine chemical structure of plant cells is still far from being well known and only slow progress is being made in the elucidation of chemical characteristics of the various morphological elements. The fibrous structures make an important contribution to texture. Plant fibers are mostly composed of cellulose and contain, in addition, other components such as proteins or pectic substances. The amount of fiber is important in many vegetables as in wax beans, for instance, where its presence is definitely undesirable. The chemical changes which occur in the pectic constituents of many fruits and vegetables can be shown to bear good relationship to the progress of softening and eventual disintegration of the cell structure.[9] These changes might be grossly described as a continuous transformation of the water-insoluble pectic constituents, such as protopectin, into soluble pectinic acids. This reaction and the associated softening were in the past ascribed to the action of enzymes present in the tissue, but there is now some doubt concerning the enzymatic nature of these changes.[37]

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* The term "flavonoid" has been suggested by Dr. Floyd DeEds of the Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, to cover both flavonols and flavonones.

The role of pectic substances in the process of maturation of many fruits such as apples, pears, peaches, and tomatoes is now generally recognized.[9] The softening effect is mostly due to the increasingly small force needed to tear cells apart or to fissure cell layers. The adhesion of such cell layers and cells to each other depends on the presence of cementing pectic materials in the middle lamella. In other words, the loss of firmness is not caused predominantly by a softening of the cells themselves, but rather by changes in adhesion.

It is only fair to state that our knowledge of the morphological and chemical factors which make plant tissue crisp, such as in celery or in eating a good apple in its prime, is very meagre. There is little doubt that pressure within the cells, as well as the presence or absence of many chemical constituents, play important parts, but the reasons for the almost endless and typical variations in the texture of various fruits and vegetables are not known.

Some textures can be measured objectively. Of the various instruments in use the pressure tester[29] is widely utilized in measuring the firmness of apples, pears, and peaches; the Texturometer and the Tenderometer[69] both used for peas and to a limited extent for some other vegetables might be noted here. None of these instruments gives an exact duplication of the type of grinding performed by human teeth and thus results obtained by such equipment and by human testers are often not in agreement.

Flavor. Almost any component of fruits and vegetables has a direct or indirect affect on the taste sensation experienced upon eating the commodity. The gross or unspecific flavor of any fruit or vegetable is usually determined by sweetness-sourness (sugar-acid) ratio. Obviously, sugars are responsible for the sweet sensation, but it should be mentioned that different sugars exhibit different extents of sweetness[12] and that the comparative sweetness of the various sugars will change as the concentrations are raised or lowered. Glucose, fructose, and sucrose are the dominant sugars in fruits and vegetables, with many others occurring in small amounts and in a restricted number of species. The "fruit acids," as organic acids commonly occurring in fruits and vegetables are often designated consist chiefly of citric, oxalic, and tartaric acids, with again a long list of other acids of lesser significance.

A definite sweetness-sourness (sugar-acid) relationship within a comparatively narrow range must exist in any food in order to satisfy the palate. A further group of compounds which play an important part in the gross or unspecific flavor effect of any plant food are the tannins.[53] These give the astringent flavor typical of many fruits and vegetables and products manufactured from them. It may be noted here that various bitter principles, mostly glucosides such as the naringin in grapefruit have a somewhat similar effect to the tannins in reducing the sweet taste sensation.

Although these compounds provide the foundation for the typical flavor of any product, such mixtures of sugars, acids, and the astringent or bitter compounds alone will never duplicate the flavor of any fruit or vegetable. In plant products there are minute quantities of various aldehydes, esters, ethers, and other compounds of usually fairly unstable nature which lend them the typical fragrance and flavor. A few of these flavoring constituents have been known for some time, but in general our knowledge of these compounds is still in its infancy. In recent years there has been considerable interest in this subject and as a result rapid progress is being made in the isolation and identification of flavoring constituents. For example, the constituents responsible for the aroma of pineapples[28] and onions are now known. It is safe to state that in most cases a complex of various chemical compounds rather than the flavor or aroma of a single chemical entity constitutes the typical flavor of a fruit or vegetable. The science of flavor classification and measurement has developed a great deal during recent years. However, no generally applicable objective methods are available as yet for the measurement of flavors.

It should also be noted that the consistency or texture of fruits or vegetables has often an important effect on the flavor sensation experienced upon eating the commodity. Little definite knowledge is available on this point.

Nutritional Value as a Quality Factor. Most people eat their food in order to provide the nutrients required for the growth, maintenance, and reproduction of the human body. A few fortunate nations have food in such abundance that the above purposes are relegated as less important, and the enjoyment of eating takes the leading role. It has been assumed in the past that in such cases as the latter, an abundant diet will automatically take care of all food needs of the body, but it is known now that this is not the case. As a result of this realization, nutritional value has been increasingly emphasized as one of the quality factors.

One may arbitrarily divide our nutritional requirements into fuel materials (calories) and of specific nutritional factors. Fruits and vegetables in the proportions consumed in this country make an important contribution toward supplying our requirements of both. Of course, the simple carbohydrates make the most important contribution in calories. Generally speaking, the fat and protein constituents of fruits and vegetables might be regarded as of lesser importance in this respect, although other plant materials such as the oil seeds and coconuts provide an increasing proportion of the world's supply of fats and oils.

Fruits and vegetables are our dominant source of ascorbic acid (vitamin C) and play a major role in supplying a long line of other essential vitamins. The chemistry of these accessory factors is discussed in detail in Chapter XXI in Volume I.

BIBLIOGRAPHY

1. Anderson, R. J., *N. Y. Agr. Expt. Sta. Bull.* 96 (1923); *ibid.* 146 (1928); Brown, W. L., *J. Am. Chem. Soc.* **62**: 2808 (1940).
2. Anonymous, "A Study of Selected Trends and Factors Relating to the Long-Range Prospect for American Agriculture." 80th Congress, Second Session, Washington, D. C., U. S. Govt. Printing Office (1948).
3. Anonymous, "Energy-Yielding Components of Food and Computation of Calorie Values." Food and Agriculture Organization, Washington, D. C. (May 1947).

3a. Anonymous, "Vegetable and Fruit Dehydration. A Manual for Plant Operators." *U. S. Dept. Agr.*, Bur. Agr. Ind. Chem., *Misc. Pub.* 540 (1944).

4. Anonymous, *Natl. Canners Assoc. Bull.* **26–L**, 7th ed. (1950).
5. Atwater, W. O., and Bryant, A. P., *Office Expt. Sta. Bull.* 28 (rev. ed.) (1906).
6. Berstein, Leon, Hamner, K. C., and Parks, R. Q., *Plant Physiol.*, **20**: 540 (1945).

6a. Blair, James S., U. S. Patent 2,189,774 (1940).

7. Blank, F., *Botanical Rev.* **13**: 241 (1947); Link, K. P., in Gilman's "Organic Chemistry" II, pp. 1315–1331. New York, John Wiley and Sons, Inc. (1938).
8. Boswell, Victor R., "Yearbook of Agriculture, 1937," p. 178. U. S. Dept. Agr., Washington, D. C.
9. Branfoot, M. H., "A Critical and Historical Study of the Pectic Substances of Plants." Dept. Sci. Ind. Res., *Food Invest. Sp. Rept.* **33**, London (1929).
10. Caldwell, J. S., *J. Agr. Research* **36**: 289 (1928).
11. Caldwell, J. S., *J. Agr. Research* **36**: 367 (1928).
12. Cameron, A. T., *Rept. Ser. No.* **9** (1947). New York, Sugar Res. Foundation.
13. Chatfield, Charlotte, and Adams, Georgian, *U. S. Dept. Agr. Circ.* **549** (1940).
14. Chatfield, Charlotte, and McLaughlin, Laura I., *U. S. Dept. Agr. Circ.* **50** (1928).
15. Cruess, W. V., "Commercial Fruit and Vegetable Products." New York, McGraw-Hill Book Co., Inc., 3rd ed. (1948).
16. Culpepper, C. W., and Magoon, C. A., *J. Agr. Research* **40**: 574 (1930).
17. Curtis, O. F., "The Translocation of Solutes in Plants." New York, McGraw-Hill Book Co., Inc. (1935).
18. Daniel, Esther, and Munsell, Hazel, *U. S. Dept. Agr. Misc. Pub.* **275** (1937).
19. Downer, A. W. E., *J. Soc. Chem. Ind.* **62**: 124 (1943).
20. Ellis, G. H., and Hamner, K. C., *J. Nutrition* **25**: 539 (1943).
21. Erwin, A. T., *Bot. Gaz.* **91**: 105 (1931).

22. Etchells, John L., and Jones, Ivan D., *U. S. Dept. Agr., Farmers' Bull.* **1932** (1944).
23. Etchells, John L., and Ohmer, Harvey B., *Fruit Products J.* **20**: 334; 357 (1941).
24. Feigenbaum, J., and Israelashvili, J. S. *Nature* [London] **159**: 32 (1947).
25. *FIAT Final Report No.* 1209, Joint Intelligence Objectives Agency, Washington, D. C. (1948).
26. Fitzgerald, G. A., "Frozen Food Technology." Frozen Food Foundation, Inc., Syracuse, New York (1946).
27. Gortner, R. A., "Outlines of Biochemistry." 3rd ed. New York, John Wiley and Sons, Inc. (1949).
28. Haagen-Smit, A. J., Kirchner, J. G., Prater, A. N., and Deasy, C. L., *J. Am. Chem. Soc.* **67**: 1646 (1945).
29. Haller, M. H., *U. S. Dept. Agr. Circ.* **627** (1941).
30. Haller, M. H., Rose, Dean H., Lutz, J. M., and Harding, Paul L., *J. Agr. Research* **71**: 327 (1945).
31. Hamner, K. C., Lyon, C. B., and Hamner, C. L., *Bot. Gaz.* **103**: 586 (1942).
32. Harding, Paul L., *Proc. Fla. State Hort. Soc.* **1940**, 78.
33. Harding, Paul L., *Am. Soc. Hort. Sci. Proc.* **45**: 72 (1944).
34. Hedrick, U. P., *N. Y. Dept. Agr. Ann. Rept.* **2**, pt. 2, 27 (1919).
35. Joslyn, M. A., and Marsh, G. L., *Calif. Agr. Expt. Sta. Circ.* **344** (1937).
36. Joslyn, M. A., and Hohl, L. A., *Calif. Agr. Expt. Sta. Bull.* **703** (1948).
37. Kertesz, Z. I., *Plant Physiol.* **18**: 308 (1943).
38. Kertesz, Z. I., Horsfall, J. G., and Rouse, A. H., *J. Agr. Research* **49**: 799 (1934).
39. LaFevre, Edwin, *U. S. Dept. Agr. Circ.* **35** (1928).
40. LaFevre, Edwin, *U. S. Dept. Agr. Farmers' Bull.* **1438** (1941).
41. Lee, F. A., and Sayre, C. B., *N. Y. State Agr. Expt. Sta. Tech. Bull.* **278** (1946).
42. Leichsenring, Jane M., Norris, Loana M., Grambow, Doris A., and Donelson, Eva G., *Food Res.* **12**: 151 (1947).
43. Loesecke, Harry W. von, "Drying and Dehydration of Foods." New York, Reinhold Publishing Corp. (1943).
44. Loesecke, Harry W. von, "Outlines of Food Technology." 2nd ed. New York, Reinhold Publishing Corp. (1949).
45. MacGregor, J. M., and Rost, C. O., *J. Am. Soc. Agron.* **38**: 636 (1946).
46. Magness, J. R., *U. S. Dept. Agr. Farmers' Bull.* **1883** (1941).
47. Mangold, E., *Nutrition Abstr. Rev.* **3**: 647 (1934).
48. Markley, K. S., and Sando, C. E., *J. Agr. Research* **42**: 705 (1931); *ibid.* **46**: 403 (1933); Chibnall, A. C., Piper, S. H., Pollard, H., Smith, J. A. B., and Williams, E. F., *Biochem. J.* **25**: 2095 (1931).
49. Mayer, F., and Cook, A. H., "The Chemistry of Natural Coloring Matters." New York, Reinhold Publishing Corp. (1943).
50. Mrak, E. M., and Perry, R. L., *Calif. Agr. Expt. Sta. Circ.* **381** (1948).
51. Mrak, E. M., and Perry, R. L., *Calif. Agr. Expt. Sta. Circ.* **383** (1948).
52. Pederson, C. S., Beattie, H. G., and Stotz, E., *N. Y. Agr. Expt. Sta. Bull.* **728** (1947).
53. Perkin, A. G., and Everest, A. E., "The Natural Organic Colouring Matters." New York and London, Longmans, Green and Co. (1918).
54. Pickering, C., "Chronological History of Plants; Mans' Record of His Own Existence Illustrated Through Their Names, Uses and Companionship." Boston, Mass. (1879).

55. Reder, R., Ascham, L., and Eheart, M. S., *J. Agr. Research* **66**: 375 (1943).
56. Saywell, L. G., and Cruess, W. V., *Calif. Agr. Expt. Sta. Bull.* **545** (1932).
57. Schroeder, C. W., and Nair, J. H., *Anal. Chem.* **20**: 452 (1948).
58. Shaw, J. K., *Mass. Agr. Expt. Sta. Ann. Rept.* **23**, pt. I, 177 (1910).
59. Shepard, C. U., *Southern Agr. Hort. Reg. Rural Affairs* (n.s.) **4**: 255 (1844).
60. Smith, M. C., and Caldwell, E., *Ariz. Agr. Expt. Sta. Mimeo. Rept.* **72** (1945).
61. Sonderheimer, E., and Kertesz, Z. I., *Food Ind.* **20**: 1300 (1948).
62. Steele, C. C., in Gilman's "Organic Chemistry II." 2nd ed., pp. 1293–1315. New York, John Wiley and Sons, Inc. (1945).
63. Stratton, F. C., unpublished data, United Fruit Co., Res. Dept., Boston, Mass.
64. Takahashi, I., *J. Okitsu Hort. Soc.* **27**: 18 (1931).
65. Tolkowsky, S., "Hesperides. A History of the Culture and Use of Citrus Fruits." London, John Bale Sons and Curnow Ltd. (1938).
66. Tressler, D. K., Joslyn, M. A., and Marsh, G. L., "Fruit and Vegetable Juices." New York, Avi Publishing Co., Inc. (1939).
67. Tressler, D. K., and Evers, C. F., "The Freezing Preservation of Foods." 2nd ed. New York, Avi Publishing Co., Inc. (1947).
68. Vavilov, N. I., "Botanical-Geographical Principles of Selection." Moscow and Leningrad. [Translation in Bur. Plant Ind., Soils and Agr. Eng., U. S. Dept. Agr., Beltsville, Md.]
69. Walls, E. P., Kemp, W. B., and Stier, H. L., *Univ. Md. Agr. Expt. Sta. Misc. Pub.* **709** (1940).
70. Whitaker, T. W., and Jagger, I. C., "Yearbook of Agriculture, 1937." U. S. Dept. Agr., Washington, D. C.
71. Wiegand, E. H., and Bullis, D. E., *Oregon Agr. Expt. Sta. Circ. Inf.* **209** (1939).
72. Wittwer, S. H., *J. Nutrition* **31**: 59 (1946).
73. Woodroof, J. A., *Ga. Agr. Expt. Sta. Bull.* **201** (1938).

Chapter III

THE CHEMISTRY OF FORAGE CROPS

J. T. Sullivan

United States Regional Pasture Research Laboratory, State College, Pa.

Unlike fruits, vegetables, and cereals, which are suitable for the human diet, forages, namely grasses, hays, straws, the entire above-ground portions of many plants, silages, roots, are available as food only to animals with digestive processes different from those of humans. Digestion in the larger farm animals, and most surely so in ruminants, is accomplished by microbiological rather than by enzymatic processes. Accordingly the availability of forages as food must not be judged on the same basis of comparison as human foods. The high proportion of difficultly hydrolyzable compounds in forage are not necessarily undesirable from a nutritional standpoint. For detailed data on composition the reader is referred to compilations which give the moisture, protein, fat, fiber, nitrogen-free extract, and mineral matter contents of forages.[6, 61, 69, 80, 86] Data on other constituents have not been compiled in such comprehensive form.

The Growing Forage Plant

The chemical composition of a forage is that of the plant from which it was derived, modified by the treatment to which it was subjected after harvest. Therefore, it may be well to review factors which affect the composition of growing plants. Most pasture and hay crops are of two plant groups—the grasses and legumes. As a result of genetic influences, the latter, at comparable stages of growth, have higher protein and calcium and lower fiber contents than the grasses. The proteins of the two groups are of similar composition, but the carbohydrates appear to be different in part. Differences between species within these two groups are minor and quantitative. The composition of all plants is affected by the stage of growth and they undergo progressive compositional changes during morphological and sexual development. With approaching maturity carbohydrates are accumulated more rapidly than is protein. The percentages of structural elements, as fibrous, cellulosic, and ligneous materials increase and protein and water-soluble substances decrease.

Other effects, but of less magnitude, have been noted as a result of one or more environmental factors not contributing to plant maturation, as time of year, time of day, moderate variations in soil moisture, soil fertility, temperature, and light intensity and duration. For example, protein in perennial plants is lower in summer than in spring or fall. Protein is higher in grass growing in shade than in grass in open sunlight. The optimum temperature for respiration is higher than that for photosynthesis, and this results in a lower carbohydrate content at temperatures above the optimum for plant growth. Translocation of carbohydrates from leaves is retarded at low temperatures, and their accumulation in the tops may be a temporary condition. Nitrates are readily absorbed at temperatures lower than optimum for plant growth but their reduction is inhibited and they may accumulate.

The influence of soil fertility on plant composition may be noted by observing the results of fertilization. Plants will absorb from the soil any elements in soluble and available form. The proportions absorbed are characteristic of the plant and of its condition and of the concentration of the element in the soil. The amount absorbed of any element essential to plant growth and the size and rate of growth of the plant are intimately associated. The addition to the soil of a moderate amount of an element which had been limiting will permit increased plant growth (or increased yield) without necessarily increasing the percentage of that element in the plant, but larger doses will promote increased concentrations in the plant.[8, 34] If plant growth is stimulated by the addition of any fertilizer a change in the composition of the plant results because of the increased proportion of young rapidly growing tissue. Similar compositional changes may be brought about by crop management practices such as grazing, mowing, or irrigation. A particular sample of forage should therefore be evaluated in the light of conditions under which it grew. For more detailed study of genetical or environmental effects the reader is referred to other sources. This chapter is concerned mainly with those constituents which enter into the chemical composition of the forage plant. Since by far the greater part of published data on forage crops has been obtained by the standard feeding-stuffs method of analysis introduced by Henneberg and Stohmann and since such data are readily available and moreover do not allow a complete appraisal of forage quality, constituents obtained by other methods of analyses will be given preferred consideration.

THE CHEMICAL CONSTITUENTS OF FORAGE

Nitrogenous Substances. *Nonprotein Substances.* Nitrogenous constituents of forage plants are usually combined under the term "crude protein." Normally about one-tenth of this crude protein is not protein but consists of free amino acids, of inorganic salts and of a number of relatively minor constituents of little importance as nutritional sources of nitrogen such as amines, other nitrogenous bases, chlorophyll, and glycosides. A complete description of these substances is not available as to their identities, quantities, or responses to genetical or environmental influences. Besides nitrates, nitrites, and ammonium salts, the presence in moderate amounts of the following has been confirmed: in ryegrass, arginine, tyrosine and tryptophan; in alfalfa, asparagine, aspartic acid, tyrosine, phenylalanine, serine, leucine, valine, alanine, stachydrine, choline, trimethylamine and betaine; in bluegrass, hydroxylamine; and from many grasses, especially in the exudate, glutamine.[55, 97] In a group of grasses containing from 17.8 to 32.3 per cent crude protein, the nonprotein nitrogen amounted to 12 to 23 per cent of the total nitrogen; 2.7 to 8.1 per cent was in amide form, 1.0 to 2.0 per cent was ammonia, and 0.1 to 4.0 per cent was nitrate.[36] High proportions of nonprotein substances are usually found in plants containing high total nitrogen percentages and rapidly growing young plants. The water-soluble nitrogen of plants (which is not the same as the nonprotein nitrogen since it may include some soluble protein) is often in excess of 50 per cent of the total when the plants are grown in water cultures where nutrients are readily available. The relative amounts of the different forms depend a good deal on the type of nutrient supplied, nitrates being present only when nitrates are furnished, and about half of the soluble nitrogen being in the ammonium form when ammonium sulfate is the nitrogen source. Boron deficiency also increases the proportion of soluble nitrogen, at least in alfalfa.

When nonprotein nitrogen exceeds 20 per cent of the total nitrogen of pasture herbage and an extreme as high as 49 per cent has been reported—such excess is always associated with digestive disturbances of the stock grazing it. High proportions are likely to occur only under special combinations of circumstances, not of long duration, as when grass suddenly commences to grow in response to heavy fertilization. A high proportion of soluble nitrogen is also associated with a very leafy growth although a lush growth alone is not necessarily indicative of this condition. Digestive disturbances such as grass tetany have been associated with soluble forms of nitrogen but the particular causal compounds have not always been ascertained.

The nitrate content of forage plants is usually less than 1 per cent of the dry weight. Soils heavily fertilized with nitrate, those in which nitrification is particularly rapid, or those under certain conditions such as deficiency of manganese will produce crops of higher nitrate content. In one case oat hay was found to contain 14.4 per cent potassium nitrate. Such amounts are toxic, and the level of toxicity depends on the quantity of forage consumed. The lower limit of toxicity has been placed at 1.5 per cent KNO_3 which is equivalent to 0.22 per cent of nitrogen as nitrate.[14, 94, 95]

The toxic effect of nitrate is not due to nitrate as such. In an oxygen-free atmosphere, as in the digestive organs of the ruminant, nitrate is reduced to toxic nitrite which in the blood stream can inactivate hemoglobin. Under acid conditions in the paunch nitrites may react with amino acids, producing nitrogen gas and leading to one kind of bloat. The symptoms of nitrate poisoning often resemble hydrocyanic acid poisoning and may be confused with it. Nitrites themselves occur to a limited extent in early spring grass and their amount is increased by heavy nitrogen fertilization.

Hydrocyanic Acid. Nitrogen-containing glycosides are those which on hydrolysis liberate hydrocyanic acid (HCN) and they are important because of their potential toxicity. Available information on these substances in grasses up to the year 1935 has been reviewed by Léeman.[49] Hydrocyanic acid has been reported in 88 grasses as well as many legumes and other forage plant families.

In the sorghums (and Sudan grass) hydrocyanic acid occurs combined in a glycoside, dhurrin, although some free HCN, not combined as a glycoside, has also been detected. When so combined the enzymes dhurrinase, or emulsin, is necessary for its liberation. Many sorghum plants appear to be deficient in hydrolyzing enzyme but usually when HCN is present enough plants containing sufficient enzyme are consumed to liberate the greater part of the HCN in 3 hours, and this is deemed sufficient to cause poisoning among cattle and sheep. Amounts of HCN have been reported to be as high as 56 mg. per 100 g. of fresh tissue in leaves and as low as 1.5 mg. in the lower internodes. A range of 6 to 350 mg. per 100 g. of dry weight has also been reported in different parts of the plant and a range of 14 to 108 in the leaves of different varieties.[32] Any variety may contain toxic amounts at certain times. Internal factors controlling the quantity of HCN are heritable and a reduction may be obtained by breeding. Sudan grass is similar to sorghum except that the amounts of HCN present are usually less and fewer cases of toxicity have been reported.[25, 32] Some writers have expressed doubt as to the likelihood of Sudan grass causing poisoning.

Two cyanogenetic glycosides occur in white clover, lotoaustralin and linamarin and they are hydrolyzed by the enzyme linamarase.[24, 56] The glycosides may exist without the hydrolyzing enzyme and vice versa. The better and more persistent strains of clover in New Zealand contained more HCN than did the poorly adapted strains and as a result the presence of HCN was made a test in seed certification. This relationship has not been observed to be true with strains in other regions. Inheritance studies have shown that the glycosides and their hydrolyzing enzyme are each conditioned by a single dominant factor with no linkage between them. Toxicity from hydrocyanic acid has not been reported in white clover.

The part that HCN plays in the metabolism of the plant is not understood. According to the theory of Treub HCN occurs as an intermediate compound during the reduction of nitrates and the synthesis of proteins and is possibly the first organic nitrogenous compound formed.[49] Any condition which interrupts the orderly conversion of HCN in protein synthesis without at the same time interfering with its formation will promote HCN accumulation. Such a condition may be brought about by any situation leading to a deficiency of available carbohydrates associated with a plentiful supply of nitrogenous nutrients. Some of the environmental influences ascribed as causes of abrupt increases in HCN are drought, frost, excessive rainfall, insect injury during drought, excess fertilizer, and variable and unusually high temperatures. Some of these influences may be controlled or avoided by proper management. It has been recommended in the case of Sudan grass that it not be pastured until it has reached a height of 18 inches or more.

Alkaloids. The alkaloids are of minor importance in pasture plants. Six have been isolated from ryegrass and the total amount varied from less than 0.005 to about 0.1 per cent, the higher concentrations occurring at times of rapid plant growth. Five have been isolated from various species of lupine.

Proteins. In most cases 85 to 90 per cent of the nitrogen of green plants is protein nitrogen. Because studies on the leaf proteins have been more recent and less intensive and because the leaf proteins have not been purified to such a degree as have proteins that have been crystallized, knowledge of them is not as complete as that of proteins from other sources. Progress in this field has been slow because of technical difficulties involved in the separation of proteins from nonprotein constituents of the leaves. Grinding fresh leaves with water and extraction with water, sometimes with the use of ether as a cytolytic agent, yields colloidal suspensions from which protein may be obtained by heating, by the addition of alcohol or salts, or by the adjustment of the hydrogen-ion concentration.[22, 70, 98]

Three groups or classes of proteins, depending upon their cellular origin, have been postulated and in some cases prepared. The first, *vacuolar protein*, was obtained by heating expressed juice of leaves and collecting the coagulum. Whether it was originally present in solution in the vacuolar fluid or had been washed out of the cytoplasm during the pressing was unknown. From the standpoint of quantity it is of minor importance, since it is usually not present in sufficient quantity to be readily obtainable. Most of the remaining protein may be brought into solution or suspension by grinding the press cake with water. From this, two more protein fractions, referred to as the *chloroplastic* and *cytoplastic* proteins, may be obtained. The former contain greater quantities of ash and lipoid material, for example, chlorophyll, and they may be separated because of their greater density and insolubility while the cytoplastic proteins may then be flocculated from solution by acid after the chloroplastic material has been removed.[22]

Although these proteins may differ in their physical properties, there is no evidence that they are different in composition, that is, in their amino acid content. Comparative analyses of the cytoplastic and chloroplastic proteins of pasture plants are not available but when proteins were prepared from the same grass by a number of procedures sufficiently different from one another to assure the presence of cytoplastic protein alone or of mixtures of cytoplastic and chloroplastic proteins in various proportions, the amino acid contents of these various preparations were found to be remarkably uniform.[51]

Yields of protein preparations depend upon the efficiencies of extractions. These are never complete, and a yield of 60 per cent of total plant proteins is the maximum which has been obtained. It has been claimed that protein material remaining in cellular debris after some proteins have been extracted is no different in composition than that which was extracted. This view is supported by a comparison of the amino acid contents of whole leaf protein preparations, that is, without separation into the different types of protein, and of the original plant material from which the proteins were prepared. In all such materials a destruction of some of the amino acids occurs during the analysis because of the presence of foreign material. However, by the analysis of certain constituents which are not destroyed, such as lysine, total organic sulfur, and amide nitrogen and under certain conditions tyrosine and tryptophan, it has been shown that the protein preparations probably have the same composition as does the whole plant on the basis of an equivalent nitrogen content. Because of the presence of fewer nonprotein impurities in the protein preparations than in the plant, the former may be analyzed for their amino acids with greater accuracy and the results should be applicable to the whole protein of the plant.

Some of these protein preparations have been analyzed for amino acids by chemical methods. The amounts of amino acids found should be taken as minimal, as many of them are no doubt underestimated. The striking result of the analyses of proteins from different plants is their uniformity in composition. Chibnall has compiled from various sources the analysis of 14 proteins, representing 8 grass and 3 legume species.[22] The differences are small and may be within the analytical errors. A fairly complete analysis of an orchard grass protein is reproduced in Table 32 (second column) from Chibnall, who compiled it from various sources. Lugg also made a compilation.[52] The latter's data concerning the range in composition occurring in grasses and in legumes are reproduced in the next two columns of the table. For comparison, an analysis of casein is given in the last column.

The leaf proteins appear to be of good quality. As the nutritional value of proteins depends on their amino acid content it is interesting to observe that the amino acids essential to animal well being, as determined with rats, are present in the leaf proteins in amounts comparable, with some exceptions, to those of casein. The amounts of histidine, leucine, lysine, and tryptophan are of the same order as those in casein. Phenylalanine and methionine are somewhat less while arginine is considerably more.

TABLE 32. THE AMINO ACID CONTENT OF LEAF PROTEINS AND OF CASEIN, AS AMINO ACID NITROGEN IN PER CENT OF TOTAL NITROGEN [88]

	Protein from Orchard Grass %	Range in Proteins of Gramineae %	Range in Proteins of Leguminosae %	Casein %
Amide N	--	4.5 - 5.4	5.2 - 5.7	-
Ammonia N	5.3	-	-	1.61
Alanine	4.4	4.4[1]	-	1.85
Arginine	15.5	13.4 - 16.4	14.9 - 15.4	3.72
Aspartic acid	4.9	4.9 - 5.4	4.7 - 5.4	5.95
Cystine	1.5	1.5 - 1.7	1.2 - 1.3	0.42
Glycine	0.4	0.4[1]	-	0.45
Glutamic acid	8.0	6.6 - 7.8	6.4 - 6.6	21.6
Histidine	2.3	1.9 - 2.6	1.6 - 2.9	2.50
Hydroxyglutamic acid	-	-	-	10.5
Hydroxy-proline	-	-	-	0.23
Leucine[2]	8.8	8.8[1]	-	9.70
Lysine	6.0	4.9 - 6.2	6.5 - 7.0	6.25
Methionine	1.3	1.4 - 1.7	1.2 - 1.3	3.25
Phenylalanine	2.5	2.5[1]	-	3.88
Proline	2.0	2.0	-	8.70
Serine	-	-	-	5.0
Threonine	-	-	-	3.5
Tryptophan	1.8	1.6 - 2.0	1.6 - 2.0	1.54
Tyrosine	2.3	2.1 - 2.5	2.4 - 2.7	5.36
Valine	4.2	4.2[1]	-	7.93

[1] Probably underestimated.

[2] No attempt was made to separate the three leucine isomers.

The high content of cystine in the proteins of wool, 13 per cent, directs attention to the necessity of an adequate supply of sulfur in the diet of sheep. This sulfur must be furnished in the organic form. The development of superior sheep capable of producing greater yields of wool has placed an extra demand upon forage for the raw materials, particularly where forage is the sole diet of the animals. It has been stated that the cystine content of a pasture might be expected to be the first limiting factor in its potentiality to support wool production. However, the possible inadequacy of pastures for wool production, as far as cystine is concerned, has not been substantiated by experiment.[22, 41] (See Chapter XVI.)

The limited information concerning the amino acid requirements of large animals and the difficulties of determining the whole amino acid content of forage render any evaluation of plant proteins on the basis of their amino acids extremely doubtful. One method of approach has been to determine the biological value of the protein under controlled tests.

Spring grass, both fresh and dried, was rated superior to fall grass for dairy cows by milk production and by the biological values of the proteins, those for spring grass being 75 to 80 per cent and for fall grass, 60 to 65 per cent. It was suggested that these differences were due to a deficiency of lysine in the fall grass and that lysine is a limiting factor in milk production. This theory has not been substantiated. The biological values of proteins in natural pastures in South Africa, as determined with sheep, were found to vary with the season of the year, being as low as 62 per cent in the spring and as high as 83 per cent in winter. The low biological values occurred when the protein content was high. The amino acid content of the proteins was believed to be responsible for the rates of growth that were obtained with rabbits fed on dried grass. A more rapid growth was obtained with timothy than with reed canary grass and was not accounted for by any superiority in chemical composition as determined. There were also strong indications of differences in the nutritive values in favor of herbage grown on fertilized soil as compared with herbage from unfertilized pastures. Although the former contained more clover there were no significant differences in the chemical composition of the two diets, but rabbits fed on the herbage from the fertilized areas grew more rapidly. The addition of cystine to the diets did not affect the results but when a mixture of cystine and casein was added the inferiority of the herbage from the unfertilized area disappeared. The differences in nutritive value of herbage from fertilized and unfertilized grass were explained partly on the basis of the amino acid make-up and it is further stated that cystine alone is not the limiting factor in the nutritive values.[41]

Virtanen's theory is that proteins in the growing plant have no fixed composition but that amino acid groups are continuously being incorporated into the protein molecule.[100] He noted that in peas and red clover the tryptophan and aspartic acid contents, in relation to total nitrogen, were higher just before blooming than during the flowering stage. It also has been reported that higher contents of cystine and methionine are present in grass that has reached or passed the flowering stage than in young grass or aftermath, or grass which has been kept short by grazing. In view of present difficulties of accurate amino acid determination these few observations are not considered sufficient to prove that proteins have a variable composition.

Digestible proteins usually amount to part of the total crude protein. The crude protein of fertilized grass has been reported as 73 per cent digestible and that of unfertilized as 68 per cent, that of young grass as 85 per cent, that of grass at the hay stage as 50 per cent, that of grass in June as 63 per cent and in the fall as 77 per cent. True protein has a lower digestibility than crude protein, the coefficients being reported as 55.6 in June and 70.8 in the fall. The digestibility of protein apparently decreases somewhat when grass is dried at high temperatures but not at low temperatures. In Vermont a drop from 76.5 to 71.0 per cent digestibility was noted on drying in a hay drier, the temperature not being specified. In Washington a drying temperature up to 350° F. caused an apparent increase in digestibility from 72.3 to 76.5 per cent but 400° lowered it to 59.2 per cent. Since it is invariably the custom to dry grass before conducting digestibility trials, little of the digestibility data that have been published on protein apply to fresh pasture grass.[27, 62, 91]

Carbohydrates. The kinds of carbohydrate substances present are numerous and not all may be described precisely. In most older publications carbohydrates are grouped into two fractions, crude fiber and nitrogen-free extract. Recently attempts have been made to describe the carbohydrates in detail since each of these fractions is composed of more than one substance.

Nitrogen-free Extract. The nitrogen-free extract is that part of the herbage which is not analyzed for directly but which is ascertained by difference. However, it is quite certain that it consists almost entirely of carbohydrates if too strict an interpretation of that term is not required. Some of its recognized components are the sugars, glycosides, starch, fructosans, pentosans, cellulose, lignin, pectins, organic acids, tannins, and some water-soluble pigments.[89] Other terms that may be met with are "soluble carbohydrates," "acid-hydrolyzable" carbohydrates, and hemicelluloses. All these are indistinguishable from one another when lumped together under the term nitrogen-free extract and there is confusion and overlapping in terminology. Some of the substances named, as the organic acids and even lignin, are not strictly carbohydrates but are included, wholly or in part, in the nitrogen-free extract.

In order to understand the carbohydrate problems and relationships it is necessary that one have an appreciation of the analytical aspects. The terminology often depends upon certain analytical procedures, not by any means well defined. While such terms as sugars, cellulose, or pentosan may connote some definite chemical substances, some of the procedures used to determine them may not be specific and the accuracy of the results or the purity of the isolated product may be open to question. Again some terms, such as acid-hydrolyzable carbohydrates or even hemicelluloses, are definitely nonspecific but are descriptive of procedures used. In the latter case the quantities obtained depend upon the conditions of the analysis which may vary with the analyst. Even when the analysis is performed under rigidly defined empirical conditions the product may vary from sample to sample. For example, in spite of the rigidly defined conditions used to determine crude fiber, its composition is not the same in different types of material. Even the term "soluble carbohydrates" may not have identical meaning to different persons, as one may use cold water, another hot and still another alcohol as the distinguishing solvent. The data in Table 33 illustrate the importance of analytical aspects in defining carbohydrate fractions.

Table 33. The Composition of Some Forage Plants with Respect to Carbohydrate Constituents.[88] (Dry Basis)

	Column Number				
	1	2	3	4	5
	Timothy Leaves %	Ryegrass Stubble %	Ryegrass Leaves %	Ryegrass Leaves %	Bromegrass Leaves %
Glucose	1.05	2.00	1.55		
Fructose	1.02	1.81	1.26		
Total monosaccharides					0.25
Sucrose	12.14	6.62	9.69		2.12
Fructosan	0.90	14.33	2.46	34.4	19.22
Starch			0.75		
Acid hydrolyzable					
Fermentable part	2.04	4.30			
Nonfermentable part	9.16	16.27			
Hemicellulose			13.29		7.00
Nitrogen-free extract				61.5	
Cellulose	18.22	27.02		23.2	
Lignin	3.88	4.03		5.1	
Crude fiber			26.5	17.1	

Glucose, fructose, and sucrose are the only true sugars commonly occurring free in plants, and they appear to be present in all plants. The first two are usually not reported separately but lumped together as reducing sugars, or monosaccharides (column 5 of Table 33). All may be reported together as total sugars. The amounts usually occurring are somewhat as illustrated with the more mature plants (column 5) containing less sugar, and with sucrose showing the most variable amounts. All sugars are also included in "soluble sugars" or "soluble carbohydrates."

Table 34. Carbohydrate Analyses of Orchard Grass Plants[88]

Part of Plant	Percentage of Plant in Each Part	In Per Cent of Dry Weight			
		Dry Matter Soluble in Alcohol	Reducing Sugars	Fructosan	Sucrose
Upper 2/3 of leaves	14.0	33.2	1.4	7.6	8.4
Lower 1/3 of leaves	12.1	23.2	1.2	22.0	5.8
Upper 1/2 of stubble	9.4	16.7	1.9	23.7	3.6
Lower 1/2 of stubble	23.6	9.4	0.7	36.2	2.6
Roots	40.9	16.5	1.2	8.2	8.9

It may be seen from analyses of orchard grass presented in Table 34, that younger plant parts contain greater quantities of the different sugars than the older ones. Interconversion of these sugars takes place by means of invertase which has both a synthetic and a hydrolytic action. The relative amounts of sucrose in relation to reducing sugars are increased when the synthetic activity of invertase is greater than its hydrolytic action. In the timothy plant glucose was in excess of fructose when the latter was being utilized in the formation of fructosan, but when the fructosan was decreasing, fructose was in excess.[75] Total sugars are higher in young grass and in grasses grown at higher fertility levels. During the cold months of the year sugars were higher in the more winter-hardy selections of alfalfa and they varied inversely as the soil temperature. Water-soluble carbohydrates are higher in grasses than in legumes. This difference is a prime factor in making grasses more suitable than legumes for silage.

Fructosans (or levulosans), anhydrides of fructose, seem to be present in all forage grasses, but not in legumes. They are sometimes referred to under various names, as triticin in *Agropyron* species, phlein in *Phleum*, graminin in *Arrhenatherum*, and levosin in *Triticum and Hordeum*.[1] The general term fructosan is more commonly used. The different fructosans found in the separate species may not be chemically identical with one another and they are not identical with inulin with which they are sometimes confused. Studies of the chemical structure of some have been made and it is believed that the fructosans of *Poa trivialis* and of barley leaves are identical and that they are anhydrides of fructose with a small proportion of glucose.[21, 39] Differences found between the fructosans of *Festuca* and *Bromus* provided a basis for changing the taxonomic classification of *Festuca gigantea*. It had formerly been placed in *Bromus* because of morphological resemblances.

Some of the properties of the fructosans, as ease of hydrolysis, make them readily included in and confused with starch. They are also included in "soluble carbohydrates" if water is the solvent but not when alcohol is used. When specifically measured they are found to occur in variable quantities, from perhaps none at all in very young leaves to considerable concentrations in certain older plant parts. They were found to increase with the growth of ryegrass, reaching a maximum of 34.4 per cent at the time the plant attained its maximum dry weight, and then decreased with the onset of maturity.[65] It is quite possible that they are converted into cellulose or other structural constituents.[67] The lower parts of the leaves and stems of orchard grass contain greater quantities of fructosans than the upper parts as shown in Table 34. In a survey of plants in Iowa a high of 7.6 per cent of fructosan was obtained in Sudan grass at the bloom stage and some fructosan was found in all grasses studied.[68] High concentrations are especially to be noted in storage parts, 33 per cent having been observed in rhizomes and roots of Canada bluegrass and 53 per cent in haplocorms of timothy.[75, 88]

Starch, an anhydride of glucose, is a normal constituent of legumes but perhaps not of foliage of grasses. Reports of large quantities in grasses are likely to be in error because of the inclusion of fructosan by improper analytical procedures. Whether both starch and fructosan occur in the same plant has not been determined. According to de Cugnac grasses which store fructosan are native to cool temperate climates and those which store starch to warmer countries.[26] Starch was reported in moderate amounts in the shoots and in somewhat greater amounts in the roots and rhizomes of some South African grasses, but fructosans rather than starch predominated in imported species.[93] If starch is present in the vegetative parts of any grasses the methods of distinguishing it from other glucosans are not often applied and may not be specific. There are evidences of the existence of other glucosans, one being a glucose-galactose polysaccharide in ryegrass.[53] Starch is included in "soluble carbohydrates" if hot water, but not cold water or alcohol, is the solvent and is included in all "acid hydrolyzable" fractions. In spite of the frequency of occurrence of starch in the vegetable world, little is known of its distribution in foliage.

There are a number of substances in plants which belong to the large class of glycosides. Of these substances, the tannins are widespread, but are important only in *Lespedeza sericea*, where they are of the catechol class. In strains of this crop, concentrations are sometimes great enough to cause bitterness and unpalatability. Variations in total tannin content of *L. sericea* have been reported from 7.5 per cent in early spring to 18 per cent in July when the plants had reached the hay stage.[23] Most of it was concentrated in the leaves. Considerable clonal differences have been found to exist, leading to the hope of reducing the tannin content by breeding.

Other glycosides associated with bitter taste and unpalatability are coumarin and related compounds. Commercial white sweet clover, *Melilotus alba*, contains 0.36 per cent coumarin, 0.27 per cent melilotic acid and 0.048 per cent coumaric acid and yellow sweet clover, *M. officinalis*, contains 0.65, 0.25, and 0.036 per cent, respectively, when analyzed at similar stages of development.[15] That bitterness is due to one or more of these seems plausible since an imported species, *M. dentata*, is free from bitter taste and contains less than 0.001 per cent of any of these substances. The coumarin of the white and yellow sweet clover varied considerably, it being higher in newly formed leaves and buds and reaching a maximum at the late-budding or early-flowering stage. Variation between plants gives hope of reducing its content by breeding. A relation was noted between the presence of coumarin and the occurrence of a hemorrhagic disease of livestock resulting from eating spoiled sweet clover hay. It has been established that the hemorrhagic agent is a decomposition product of coumarin.

Saponins may be widespread but only in alfalfa have they been reported in appreciable quantities.[44] Alfalfa saponin, although chemically similar to other saponins, does differ somewhat in that it does not hemolyze blood and also contains nitrogen, a characteristic which places it as a connecting link between true saponins and alkaloids.

Structural Substances. Preparations of crude fiber from various types of forage were found to contain on the average 85 per cent cellulose and 12 per cent lignin.[64] Since lignin ranged from 2 to 20 per cent its proportion does not seem to be fixed. Moreover only 4 to 67 per cent of the total plant lignin and 40 to 88 per cent of the total cellulose were found in the fiber. From another source fiber was found to consist of 96 per cent natural cellulose and 4 per cent of lignin. These were only part of their total in the grass.[50]

Cellulose, which comprises the framework of the plant, is a glucose anhydride, but naturally occurring cellulose is encrusted with other substances. This encrusting material is not uniform but varies with different plants and the amount increases with age and maturity. Most but not all the cellulose is found in the crude fiber and probably very little in acid-hydrolyzable material.

The encrusting substances on cellulose are of two categories, the hemicelluloses and lignin. While more than one type of hemicellulose exists, those in forage plants appear to be of the polyuronide type, i.e., when hydrolyzed they yield, in addition to simple sugars, uronic acids. Hemicelluloses of sheep fescue and sweet vernal grass contain arabinose and xylose, both pentoses, and an unidentified uronic acid.[11] Those of alfalfa consist chiefly of xylose, a small amount of arabinose and a uronic acid.[74] In the roots of alfalfa the hemicelluloses consist of glucose and xylose and probably glucuronic acid.[18]

The importance of analytical procedures is nowhere more evident than in determining the amount of hemicellulose. In Table 33, columns 1 and 2, the figures for acid hydrolyzable material represent at least part of what might be determined by another analyst as hemicellulose. The fermentable part of this is probably chiefly glucose and the nonfermentable part pentoses (arabinose and xylose). In obtaining the data shown in column 3 the material was treated with a different concentration of acid than was the case in obtaining the data shown in either column 1 or 2. The sugars produced by the former method were measured as if they were only glucose. In some cases the pentoses, including uronic acids, are measured by determining their furfural content, and the results are reported as pentosans; in other instances the hemicellulose is dissolved out and weighed. In all these cases slightly different substances are included in the term hemicellulose.

The other chief contaminant of cellulose, and of hemicellulose as well, is lignin. Although usually considered with carbohydrates its structure is unknown. It is characterized by its resistance to attack by many chemical treatments and also by microorganisms. The amounts found in plants depend to a great extent on the analytical procedures used.

Pectins are minor constituents in the grasses, amounting to 1 per cent or less in bluegrass and located in part in the middle lamella of cell walls.[10] In constitution they are similar to hemicelluloses, being composed in part of pentoses and uronic acids. What knowledge there is available regarding pectins does not come from forage plants but from other plants where they occur in greater quantity. Unless a separate analysis for them is made they may be included in the hemicelluloses.

Close relationships are believed to exist between pectins, hemicellulose, and lignin. In very young cells cellulose appears to exist in union with protein or fatty acids. As the cell ages the cellulose becomes associated with other carbohydrates instead. The sequence of formation of these other carbohydrates determines the composition of the plant at various stages. Pectin, hemicellulose and lignin, in turn, are of importance. All three are present in the mature or lignified tissue. The theories of their formation have been summed up by Norman.[66]

Significance of Carbohydrates to Plant and Animal Nutrition. It would be well to point out here that the carbohydrates of forage crops have relationships to fields of study covered elsewhere in these volumes. (See Chapters XIII to XVIII.) In perennial plants the carbohydrates, especially of the lower and underground parts, are considered as reserves to be utilized in the development and to aid in the survival of plants which have been subjected to severe climatic conditions or to excessive cropping or defoliation.[34, 35, 92] Also the carbohydrates, as the chief sources of energy to farm animals, are being studied intensively from the standpoint of their susceptibility to the digestive processes.[13, 50]

Crude Fat or Lipids. Crude fat is composed of substances extractable by ether but all fatty substances are not readily soluble in ether alone. The word lipids has been suggested. True fats, which are glycerides of the fatty acids, are only a part of the total. Thirty-six per cent, on the average, of the crude fat of various hays and fodders have been reported as saponifiable and since the true fats are only a part of the substances capable of being saponified the true fats would be of even less magnitude.[33] The coefficient of digestibility of the saponifiable portions of the hays was 66 and most of this was due to the true fats. The unsaponifiable part was only 29 per cent digestible. It is obvious that only part of the crude fat is of high energy value.

Total lipids in orchard grass were reported to average 6.12 per cent and the fatty acids, chiefly but not entirely derived from the true fats, 3.13 per cent.[82] The fatty acids consisted of acids of 14 or more carbon atoms. Three-fourths of them were unsaturated acids with 18 carbon atoms while only one-sixth were of the saturated series. In another report on the same species 67.5 per cent of the fatty acids were reported as of the 18 carbon unsaturated series, as follows: 29.5 per cent alpha-linoleic, 16 per cent beta-linoleic, 16 per cent alpha-linolenic and 6 per cent beta-linolenic.[84] The common oleic acid was not found. The saturated acids were mainly palmitic and stearic.

As grass matures both crude fat and total fatty acids decrease. The iodine number of the acids also decreases. Perhaps as a result, the oleic acid of butter fat is lower when cows have been fed on hay rather than on grass.

Nonfat constituents of the lipids are varied and consist in part of phosphatides, waxes, wax alcohols, or sterols, perhaps other alcohols and hydrocarbons and the fat-soluble pigments. While the true fats are probably completely digestible, many of these nonfats seem to be completely undigestible and few are of any food value. Phosphatides will be discussed under compounds of phosphorus. Only part of them are included in the crude fat as they are with some difficulty completely dissolved in ether. The fatty acids of the phosphatides are, like those of the fats, chiefly linoleic and linolenic.[84]

The waxes which have been identified are the esters of *n*-hexacosanol in orchard grass and ryegrass and of *n*-triacontanol in alfalfa.[77] The alcohols which occur in waxes, the sterols, are also found free. Two forms of medicagosterol were found in alfalfa, one of which may be identical with alpha-spinasterol, also in alfalfa.[29] Sitosterol and possibly a very small amount of ergosterol were found in orchard grass.[76] The sterols, not all of them however, and not necessarily those identified, are the substances which on exposure to ultraviolet irradiation assumes vitamin D activity.

Other substances identified in forage plants are the hydrocarbon triacontane in alfalfa, hexenol, a fragrant alcohol in white clover and the plastid pigments. The plastid pigments are of two groups, the chlorophylls and the carotenoids, the chemistry of which has been discussed in Volume I, Chapters IX and X. These compounds are closely associated, occurring in the same cells, together determining the color of the leaf and perhaps having an associated role in photosynthesis. They are chemically dissimilar, however, the two chlorophylls, designated as a and b, being saponifiable and containing nitrogen and magnesium and the carotenoids being either hydrocarbons, as the carotenes, or slightly oxygenated hydrocarbons, as the xanthophylls. Miller quotes the following approximate relationship: chlorophyll a two parts, chlorophyll b three-fourths of one part, carotene one-sixth of one part, and xanthophyll one-third of one part per 1000 parts of green leaf.[57] In 76 clonal lines of bromegrass, fully headed, total chlorophyll ranged from 54 to 211, total carotenoids from 10.2 to 30.3, and carotene from 3.4 to 12.4 p.p.m. of the dry weight. In

55 clones of crested wheat grass total carotenoids ranged from 13.1 to 32.0 p.p.m. and carotene from 3.8 to 10.5 p.p.m.[45] Chlorophyll and carotene were quantitatively related as shown by the fact that significant correlations were found in the wheat grass between chlorophyll and total carotenoids and between chlorophyll and carotene. In white clover the chlorophyll-carotene ratio varied during a year from 18 to 98 and averaged 36.2, the chlorophyll-xanthophyll ratio averaged 12.5 and the xanthophyll-carotene ratio 2.9.[5]

No direct nutritional value of chlorophyll to animals has been noted. However, a deep green color of foliage, indicating high chlorophyll content is usually correlated with high protein and high carotene. A correlation between chlorophyll and yield has been sought in some crops but was not observed in crested wheat grass and bromegrass.[45] Like chlorophyll, the xanthophylls, of which six have been detected in the higher plants, have no known nutritional value. Some of the carotenes, however, do have nutritional value and will be discussed later.

The Vitamins of Forage Crops. Although the vitamins have been discussed in detail in Chapter XXI of Volume I, their occurrence in forage crops is so important that a brief discussion will be given here.

Carotene (Provitamin A). Vitamin A does not occur in growing plants. Instead one finds its precursors which are members of the carotenoid group, particularly alpha- and beta-carotene. Alpha-carotene is relatively insignificant in quantity, amounting, according to one source, to only 0.7 per cent or less of the total carotenoids and having only one-half the vitamin A activity of the beta isomer which makes up the bulk of the carotenes. Other isomers have been reported of uncertain identity and terminology which may or may not exist in the living plant but which may have arisen from beta-carotene preliminary to or during the process of analysis. For example, 72.7 per cent of the crude carotene of some Texas grasses was beta-carotene but the beta-carotene equivalent was 77.1 because some of the other carotenoids had partial vitamin activity.[46] The beta-carotene content of the crude carotene of fresh grass clippings in England was 97 per cent but only 66 to 79 per cent when the same grass was dried.[48] Similarly a percentage of 85 has been reported in alfalfa hay.

The concentration of carotene is relatively high in young plants and decreases as the plants age and become stemmier. The content of four species of grasses averaged 490 p.p.m. at the "short grass stage" of development and decreased regularly to 132 at seed formation. A mixed herbage dropped from 381 p.p.m. to 101 between April and July. First crop alfalfa contained 432 p.p.m. of carotene when 5 inches high and only 171 when 31 inches high and in half bloom. The succeeding cuttings followed a similar pattern, beginning high and falling to a lower level when ready for another cut. The aftermath, unless harvest was delayed too long, was higher than the hay cut.[88]

Leaves are usually higher in carotene than other parts of the plant. In one study of grasses the leaves had 3 to 11 times more carotene than stems.[81] With alfalfa the ratio of carotene in the leaf to that in the stem showed a tendency to rise as the plant developed, suggesting that deterioration in the stem was comparatively more rapid than in the leaves. On the other hand, ryegrass was found to have less carotene in the leaves than in the heads and flowers.[83]

A few studies have been made but are not in agreement as to the carotene contents of successive cuttings of grass during a season. Clovers are in general higher than the grasses and do not display a low summer minimum common to most grasses. The drop in carotene that grasses display during flowering is not so evident in white clover. In this respect white clover may be like other legumes, such as peas, with the carotene contents highest at flowering time.[99] The more extended flowering period of white clover may be a factor in upholding the carotene content of mixed herbage during summer. Moreover a pasture mixture at any one time contains a conglomerate of types with respect to steminess and leafiness, and, even though carotene in each tends to diminish as the plants approach maturity, no sharp changes in the carotene content of the mixture may be expected.

According to a few observations soil fertility has an effect on carotene content, perhaps by controlling the production of new tissue. In one pasture of mixed herbage ammonium sulfate fertilization increased carotene from 434 to 580 p.p.m. and lime increased it to 482.[17] In another trial both ammonium sulfate and nitrate of soda applied at monthly intervals caused average increases of 28 per cent in carotene while potash increased it 6.2 per cent. In another trial, ammonium sulfate raised carotene of ryegrass leaves 55 per cent and that of the heads 17.7 per cent.[83] Carotene content of plants is reported to be reduced by drought and by high midsummer temperatures in combination with drought.[4] Insect pests and diseases may cause severe losses because they attack plant parts highest in carotene.

It has been noted that carotene is correlated with chlorophyll and both of them with protein. Dark colored clones of orchard grass were noted to be higher in carotene than lighter colored ones. The relationship between carotene and protein is close, some correlation coefficients having been reported as 0.53, 0.85, and 0.89.[17, 59, 83]

The relation of palatability and vitamin A content has been studied in six grasses and three legumes.[2] Without exception palatability was directly related to vitamin A content. The high carotene content of green forages renders them fit sources of vitamin A for supplementing other feeds. Alfalfa leaf meal, in particular, is the commercial source of crystalline carotene as well as of xanthophyll, chlorophyll, and sterols.[60]

Other Vitamin Substances. Specific determinations for the vitamin B group have been made in forage plants. Dried young grass (oats) contains in parts per million, thiamine 2 to 13, riboflavin 14 to 27, biotin 1.5 to 2.2, pantothenic acid 13 to 18, and nicotinic acid 60 to 90.[47] They are in general at maximum concentration at or about the jointing stage. Alfalfa contains thiamine and riboflavin which decrease in concentration as the plants mature and are in general correlated with leafiness, greenness, and protein content. The riboflavin content of dried grasses and hays are: bluegrass 10, alfalfa 9 to 16, and timothy 12 to 17 p.p.m.[42] The nicotinic acid content of different hays is 35 to 48, of bluegrass pasture 66, and of alfalfa pasture 93 p.p.m.[37]

Vitamin C, or ascorbic acid, appears to be generally present in all green forage. In alfalfa it is most concentrated in the leaves, next in the petioles and least in the lower stem. It attains its maximum in young alfalfa just reaching the budding stage and during cool weather, dropping to one-half or one-third the maximum in hot weather. The grass juice factor is alsc present in the green plant. It, with other B and C vitamins, seems to be unimportant as a limiting factor in the diet of grazing animals.

Vitamin D seems to be absent in fresh pasture. Grazing animals must obtain their needs for this vitamin from sunlight or from sun-cured hay, during the drying of which certain sterols, under the action of the ultraviolet rays of sunlight, take on vitamin D activity. Vitamin E is present in all green herbage in amounts probably ample for grazing animals. Vitamin K has been isolated from the lipide fraction of alfalfa but so far has been demonstrated of importance only to the chick and to the rat. In them it is antagonistic to the hemorrhagic effect produced by the coumarin compound formed in spoiled sweet clover hay.

Minerals. The amount of total ash in growing forage is quite variable. For example, in a series of 17 samples of grass, each sample being a composite of a year's clippings from a single pasture, total ash varied from 7.68 to 17.88 per cent of the dry weight, with an average of 11.68 per cent.[28] The composition of the ash is, however, of more importance than the amount, as part of it consists of minerals such as silica of no nutritional importance. Sometimes in addition to, or instead of, total ash, the soluble or the insoluble ash is reported, the former being a measure of that part of the total ash soluble in either water or dilute acid and the latter being a rough measure of and containing all the silica. Since silica may also be included in a grass sample by soil contamination the amount of silica-free ash should be a better measure of the presence of essential minerals than total ash. For the 17 samples referred to above, the soluble ash, calculated from the data, was found to range from 4.05

to 8.70 per cent, with an average of 7.00 per cent. Soluble ash showed a greater correlation with some of the minerals than did the total ash, the coefficients for the soluble ash with calcium and phosphorus being 0.48 and 0.49, respectively, while the corresponding coefficients for the total ash were − 0.24 and − 0.06. The reader is referred to Chapter VIII in Volume I for a general discussion of inorganic materials in plants.

Calcium. Calcium is a variable plant constituent. Yearly averages of clippings from a number of pastures in one locality varied in one year from 0.59 to 0.97 per cent calcium and in another year from 0.64 to 1.08 per cent.[28] Individual samples from a larger number of pastures scattered over a wider area ranged from 0.28 to 1.74 per cent calcium.[63] The average of all was 0.82 per cent. From another locality is reported an average of 0.57 per cent for herbage from pastures and fertilized plots.[3] Orr reported an average of 1.10 per cent calcium for 48 "cultivated" pastures in England, 2.47 per cent for a single paddock where race horses had been grazed and which had been manured intensively, and an average of 0.29 per cent for pastures in the Falkland Islands.[69]

Two important factors control the calcium content of herbage and are responsible for these variations, namely, floral composition and soil fertility. Legumes, as compared with grasses, are relatively higher in calcium as they are in protein. In mixed herbage therefore the presence of legumes will increase both the calcium and protein contents, and correlations have been found between these two constituents.[69]

Calcium seems to have a number of functions in the plant. One is the neutralization of acids, especially of oxalic acid. In legumes which have a higher nitrogen metabolism than grasses, more lime is required to neutralize the organic acids formed and a higher calcium-nitrogen ratio is present. Other functions of calcium are not so well understood. Forty per cent of the calcium in alfalfa hay is water-soluble and, judging by its oxalate content, about half of the remainder, or one-third of the total calcium, is in an insoluble form other than oxalates. The association of calcium with structural carbohydrates has already been mentioned.

There are certain geographical areas in which the calcium content of forage is low enough to cause deficiency diseases in animals, but such deficiencies should not occur when legumes are present.

Phosphorus. In the group of pastures previously mentioned, phosphorus in the herbage ranged from 0.28 per cent to 0.50 per cent with an average of 0.37 per cent for one year and from 0.14 per cent to 0.54 per cent with an average of 0.28 per cent in another year. In another group of pastures it ranged from 0.16 to 0.57 per cent with an average of 0.30 per cent. Western Massachusetts pastures averaged 0.19 and fertilized plots in that state 0.33 per cent. For "cultivated" pastures in the British Isles Orr reports the phosphorus content as 0.74 per cent, for "natural pastures" 0.67 per cent, for "poor hill pastures" 0.24 per cent, for the Island of Lewis 0.24 per cent, and for the Falkland Islands 0.54 per cent.[69]

In contrast to calcium, phosphorus is present in about equal quantities in grasses and legumes, and its content in herbage seems to be influenced more by soil fertility than by any other factor. Its presence is correlated even more closely with protein than is calcium. Correlation coefficients were reported for the cultivated English pastures of 0.85 ± 0.04 and for the Falkland Islands pastures of 0.87 ± 0.04.[69] These high correlations in the case of phosphorus may be attributed in part to the close association between protein and phosphorus compounds in the plant. The nucleoproteins, a group of proteins present in all cell nuclei of both plants and animals, contain phosphorus, perhaps from 0.5 to 3.0 per cent.[30] These nucleoproteins, on hydrolysis, yield simpler proteins and nucleic acid, the latter containing all the phosphorus, amounting to 8 to 10 per cent of the nucleic acid. Other phosphoproteins may be present. About 20 to 30 per cent of the total phosphorus of ryegrass was classed by Chibnall as "firmly-bound protoplasmic phosphorus" and therefore probably protein phosphorus.[22] It also occurs in the protoplasts as phosphatides which may be present in amounts as high as 5 per cent.[78] Several of the phosphatides have been identified in grasses, as lecithin, perhaps a constituent of all living cells, and as cephalin. Other minor phosphorus-containing substances are phosphatidic acid, hexose-phosphate and phytin, as well as inorganic phosphates.[84] Phytin is an ester of phosphoric acid and inositol, the latter a growth substance for microorganisms. In all organic combinations phosphorus is present as the salt or ester of phosphoric acid which may readily be obtained from them by simple hydrolysis. Heating leaves to 85° C. may render the whole phosphorus content soluble in water.[31] Inorganic phosphates are usually soluble in the cell sap. About half of the total phosphorus in alfalfa hay was found to be inorganic and about 75 per cent water soluble.[57]

Animal requirements for phosphorus are not met on a diet of herbage alone in many areas throughout the world. Phosphorus-deficiency diseases are found, more frequently in cattle than in sheep, partly because the requirements of cattle are higher and partly because cattle are less able than sheep to graze selectively those younger parts of plants which are relatively richer in phosphorus. Calcium deficiency and phosphorus deficiency sometimes occur together.[7, 79] (See Chapters XIII, XIV, XVI, and XVIII.)

Other Minerals. The potassium content of forage plants is usually between 1 and 3 per cent, the amount decreasing with the age of the plant and controlled in most part by quantities available in the soil. Legumes are somewhat higher than grasses, an extreme of 7.51 per cent having been reported in white clover.[6] No definite compound of potassium has been identified in plants other than inorganic salts, practically all of which are soluble in water. Deficiency of potassium for animal needs occurs very rarely. Although essential to both plants and animals, potassium is of interest more from the standpoint of plant nutrition than from animal requirements.

Sodium and chlorine, like potassium, probably occur only as inorganic salts in herbage.[69] Twenty-four British pastures averaged 0.25 per cent sodium (Na_2O) and 0.95 per cent chlorine. Such extremes have been reported, however, as 0.02 per cent and 1.76 per cent of sodium in alfalfa, 0.02 per cent and 0.57 per cent sodium in timothy, 0.20 per cent and 0.66 per cent chlorine in alfalfa, and 0.20 per cent and 1.46 per cent chlorine in white clover.[6] Plants rarely meet the animal requirements in either of these elements.

The magnesium content of 19 species of grasses, mostly western grasses, ranged from 0.06 per cent to 0.32 per cent, with an average of 0.16 per cent. Six mature legumes averaged 0.38 per cent. Sudan grass contained 0.53 to 0.70 per cent Mg as MgO. The percentages decrease as the plant matures. The greater part of magnesium occurs in the plant as an inorganic salt and, other than salts, chlorophyll is its only recognized compound. The possibility of a magnesium deficiency in animals is remote.[57]

Sulfur is high in young rapidly growing plants and tends to decrease late in the growing season. Its content in pastures has been reported as ranging between 0.20 and 0.69 per cent in Scotland and between 0.09 and 0.40 per cent in South Dakota.[69, 72] There is little difference between herbage from good and poor pastures with respect to sulfur content, and there is no correlation between sulfur and other mineral elements. The legumes, especially alfalfa, are slightly higher than the grasses. Much of the older data that have been published for sulfur are low because of losses during analysis by improper methods of ashing.

Sulfur occurs as inorganic sulfates and as a constituent of proteins and of volatile organic sulfur compounds. The last have not been demonstrated to be present in sufficient amounts to be of any importance in forage plants. Protein sulfur occurs in three amino acids, cystine, cysteine, and methionine which have been discussed with the proteins. A deficiency of sulfur in pasture plants for animal needs has not been demonstrated. Inorganic sulfates may account for a considerable part of the total sulfur in plants where there is an ample supply in the soil but such a form of sulfur is of no value to the animal.

Iron is a very small part of the plant minerals. Grass clippings from plots contained between 0.02 and 0.39 per cent iron with species averages between 0.04 and 0.10 per cent. Orr lists species averages between 0.01 and 0.10 per cent, the legumes being all above 0.04 per cent and the grasses all below 0.05 per cent.[69] Distinction may be made between the total iron and the soluble iron. In white clover, for example, it has been reported that leaves contained 0.057 per cent total iron, whereas the iron of the expressed juice amounted to 0.028 per cent. The corresponding figures for the stolons were 0.021 and 0.003 per cent.[43] Because of the high iron content of soils as compared with that of plants, soil contamination may materially augment the iron content of the sample and many of the higher figures reported may be a result of such contamination. Another source of contamination which may increase the apparent iron content is the grinding machinery used in the preparation of the plant material for analysis.

The iron requirements of farm animals are believed to be well below that usually supplied by forage. Many stock diseases have from time to time been attributed to iron deficiency, and some have been corrected by the administration of iron salts to the animals, sometimes large doses being required. It is now recognized that some of these diseases are the result of cobalt, rather than iron deficiency and the correction was obtained by the traces of cobalt present as an impurity in administered iron salts.

The copper content of forage is roughly one-tenth that of iron, averages of 5 to 14 p.p.m. having been reported for different pasture species.[7] Spectrographic analyses showed a range of 33 to 64 p.p.m.[16] These are ample amounts for animal requirements, but occasional soils are so deficient that disturbances are likely to occur.

Cobalt is not an essential plant mineral but is of importance because of its apparent essentiality to ruminants. The average cobalt content of the herbage of pastures considered healthy to ruminants is 0.106 p.p.m. while those considered deficient averaged 0.038 p.p.m.[79] Pasture forage containing less than 0.07 p.p.m. are unhealthy for sheep and those containing less than 0.04 p.p.m. are unhealthy for cattle. In some areas symptoms of cobalt deficiency occur only in late winter when hay is fed, hay containing less cobalt than fresh grass. The cobalt content of forage is not always related to the total cobalt content of the soil but in general New Zealand soils containing less than 2 p.p.m. of cobalt produced cobalt-deficient forage. American soils range higher, from 5.0 to 16.0 p.p.m. of cobalt (personal communication, K. C. Beeson) but a number of deficient areas have been identified.

Iodine occurs both as inorganic iodides and as a constituent of organic compounds though none of the latter have been specifically identified in forage plants. Total iodine has been found in quantities as high as 5 p.p.m. but much lower amounts are more common, such as 0.19 in clover, orchard grass, and meadow fescue, and 0.27 in meadow foxtail in England, 0.16 in alfalfa, 0.07 in timothy, and 0.09 p.p.m. in redtop in the United States.[7, 79]

The importance of iodine lies entirely in the requirement that the thyroid gland of an animal must maintain a critical level of iodine or else the enlargement known as goiter will result. This level is not maintained by forage alone in many areas. In Oregon slight goiter occurred in areas where the alfalfa hay contained 0.075 to 0.100 p.p.m. and severe goiter when the hay contained only 0.045 p.p.m. In Germany the hay from a farm on which dairy cattle were goitrous contained 0.041 as compared with 0.062 p.p.m. of iodine in hay from a goiter-free farm.[58, 79] A map showing deficiency areas in the United States has been reproduced by Beeson.[7]

The manganese content of grasses showed a range of 78 to 207 p.p.m. in Idaho, of 180 to 520 in Maryland, and of 32 to 450 in Illinois. It is noticeable that orchard grass tends to be higher than other grasses in manganese.[12, 16, 85] Legumes tend to be lower than grasses, perhaps because soil conditions suitable for the growth of legumes, such as the presence of lime, render soil manganese less available to the plant. Amounts found in plants are also dependent on soil management.

The amounts of manganese usually found in forage are above animal requirements. In many areas, however, plant growth has responded to manganese application, an indication that a deficiency does occur with respect to certain crops. Deficiencies to the grazing animal have not been definitely proved, although such a possibility exists. On the other hand, an excess of manganese is possible. Areas which produce forage with large amounts of manganese are areas in which horses are subject to anemia. In an anemia-free section of Sweden, hay from plowed lands averaged 57 p.p.m. of MnO and that from uncultivated land 344. Where anemia occurred in a neighboring area the corresponding figures were 164 and 642. In anemia districts, but on land where no actual cases occurred, the hay contained 166 and 443 p.p.m., respectively. It has been proposed that anemia was caused by thiamine deficiency in hay occasioned by the excess of manganese. It has also been noted that the manganese content of pastures in districts where lactation tetany is prevalent is higher than that where tetany has not been found. Twenty-three forage samples from a diseased area ranged from 50 to 1320 and averaged 734 p.p.m., while 24 samples from a healthy area ranged from 16 to 109 and averaged only 59.[79]

Large amounts of molybdenum have been found in the teart pastures of Somerset, England, where cattle and sheep suffered from excessive scouring. Healthy pastures contained less than 5 p.p.m. of molybdenum while teart pastures contained 30 to 80. Higher than normal amounts of molybdenum have been reported in Australian pastures in localities in which bovine hematuria or "red water" occurs.[79] High concentrations have also been reported in vegetation in Wyoming, but the effects may be obscured by selenium toxicity.

Selenium as a forage constituent occurs only in certain parts of western United States, western Canada, and Mexico. The amount present in plants depends on the kind of plant and the amount and form of selenium in the soil. The native range grasses do not absorb excessive amounts of selenium except under unusual circumstances but a concentration of 4 p.p.m., the tolerance limit for cattle and sheep, is often exceeded. Alfalfa containing 100, wheat grass 36, and feather grass 24 p.p.m. of selenium have been reported. Certain weeds have been found to contain several hundred parts and may reach as high at 4000 p.p.m. Selenium exists in soil in the form of selenates which are readily available to all plants and also in the form of selenites, which are available only to the so-called seleniferous weeds. On the death and decomposition of these weeds the selenium is returned to the soil in the form of selenates which are readily taken up by near-by grasses.[19, 79]

The boron content of forage ranges from about 10 p.p.m. upward, depending on the amount of available boron in the soil. It is essential to plants but not to animals. The growth of alfalfa is often limited by the boron supply.

HARVESTED FORAGES

Processing of Hay and Silage. *Time of Cutting.* The time of harvesting, in relation to the stage of plant growth, is the most important single factor influencing the percentages of the major components of any kind of hay or silage. Plants undergo progressive compositional changes during the process of maturation. Early cut grass is higher in percentages of moisture, protein, total ash, phosphorus, and carotene. Later cuts are higher in cellulose, pentosan, lignin, and calcium. Water-soluble carbohydrates increase and then fall, the maximum in ryegrass occurring at the time of full emergence of the head. Crude fat, true fat, and the iodine number of the fatty acids decrease with maturity. The digestibility of all components falls, particularly at the more advanced stages. Exceptions occur with certain seed-forming crops such as corn and soybeans in which quantities of highly digestible proteins and carbohydrates are deposited in the developing seeds. It is advantageous therefore to cut for hay when the maximum amount of digestible nutrients are present, and with consideration of the mineral and vitamin contents. Late cuts are undoubtedly lower in quality, whereas early cuts yield less total dry matter. In cutting for silage it is necessary to consider the importance of readily fermentable carbohydrates, which are obtained in grasses at relatively earlier growth stages than those giving maximum hay yield. The earlier the cut the greater the carotene or vitamin A activity.[41, 61]

Hay Drying. Making hay is the process of reducing the water content of cut forage so that it may be stored without spoilage and it is an objective to do this with a minimum loss of nutrients. For most forages the water content must be brought from 65–80 per cent to below 22 per cent. Some of the known changes that take place which may alter the composition and quality of the feed are hydrolysis of carbohydrates by enzyme action, oxidation of carbohydrates, fermentation of carbohydrates by plant respiration and by microorganisms, destruction of carotene, loss of minerals and other soluble nutrients by leaching, and loss by shattering. The degree of loss depends on one or more of such factors as rapidity of drying, temperature, source of heat, aeration, and light. Spoilage, caused by rainfall or overheating while wet, causes greater and more varied changes than drying alone. The oxidation of fats and the denaturation of proteins may not be of great nutritional importance. Lignin increases quantitatively at certain high temperatures. Vitamin D activity is present only after the cut forage is exposed to sunlight.[90]

Slow drying in the sun may cause losses up to 40 per cent of total dry matter with corresponding losses in many of the major constituents. The higher rates of loss usually occur in unfavorable drying weather when fermentation and leaching are major factors. Losses are less under artificial drying, especially when the drying rate is accelerated by heat. The rate of temperature rise rather than the temperature attained determines the loss of carbohydrates by enzyme activity and respiration. The temperature attained is a factor in loss of carbohydrate by oxidation, losses occurring at any temperature above 80° C.[41]

Drying also affects digestibility. With mixed herbage the coefficients of the major constituents increased with drying temperatures up to 177° C. (350° F.) but not at 204° C. (400°F.).[40] The highest temperature will decrease protein digestibility. Further losses occur during storage, principally in the nitrogen-free extract and to a lesser degree in the lipides. Excess moisture during storage will promote spoilage and spontaneous combustion.[20]

The carotene content is considered the best single criterion of hay quality. Market hays will contain from nothing up to over 100 p.p.m. of carotene.[96] The higher carotene hays are those cut at an early plant stage when the plants were in a leafy condition and consequently relatively high in protein, minerals and digestible carbohydrates. Low carotene indicates mature cutting or improper curing. Losses of carotene are much greater during sun drying than under artificial heat. It is claimed that the destructive agent is a lipoxidase present in the leaves which is inactivated under artificial drying conditions.[88]

Silage. Forages may be preserved by the products of their own fermentation. When green fodder is sealed from contact with air, cell respiration depletes the oxygen and produces conditions suitable for the growth of anaerobic organisms, mainly of lactic acid-producing bacteria. Volatile and nonvolatile acids and alcohol are produced at the expense of sugar originally present and of sugar derived from hydrolysis of part of the starches and pentosans. Proteins are in part hydrolyzed to proteoses, peptones, and amino acids, which are deaminized with the formation of ammonia. The reactions proceed until arrested by the accumulated acid. A sample of corn silage with a pH of 3.8 contained 67.9 per cent moisture, and, on a dry basis, 0.9 per cent alcohol as ethyl, 1.2 per cent volatile acid, and 8.0 per cent nonvolatile acid, three-fourths of which was lactic. It contained 1.2 per cent nitrogen, nearly half of which was soluble and one-fifth of which was of free amino acids.[73] There was a loss of about 10 per cent in total dry matter during the fermentation, mostly in the first few weeks. In the ensilage of such forage as grasses and legumes which contain less readily fermentable carbohydrate than corn, there is often insufficient lactic acid produced to prevent spoilage. With such materials lactic acid production may be increased by an admixture of carbohydrate to the fodder when placed in the silo in the form of molasses, ground cereal grain, corn fodder, milk whey, or other high carbohydrate material or mineral acids may be added as preservative. The amount of carbohydrate or of mineral acid added should be sufficient to increase the acidity, after fermentation, to a pH of 4.0 or less. An alfalfa silage made with no added preservative had a pH of 4.53, contained 3.6 per cent lactic acid, 5.2 per cent acetic acid and was of poor quality. The addition of 40 pounds of molasses per ton of alfalfa gave a silage of pH 3.98, and containing 10.8 per cent lactic acid, 2.5 per cent acetic and was rated excellent in quality.[87] Silages of similar composition as regards the major nutritive components may be obtained by the addition of a mixture of hydrochloric and sulfuric acids (A.I.V. method) or of phosphoric acid. The production of lactic acid by fermentation is still desirable for good silage even when mineral acids have been added.[9, 20, 71]

The production of good silage is usually attendant with lower losses of nutrients than is the making and storage of hay and is particularly of advantage in preserving the carotene value, little of which is lost in the process. Increases that are occasionally observed in the vitamin A content of silage may be only apparent because of the greater availability of carotene to extractive agents after fermentation. The composition of hays and silages have been published in detail elsewhere.[61, 80]

BIBLIOGRAPHY

1. Archbold, H. K., *New Phytologist* **39**: 185 (1940).
2. Archibald, J. G., Bennett, E., and Ritchie, W. S., *J. Agr. Research* **66**: 341 (1943).

3. Archibald, J. G., Nelson, P. R., and Bennett, E., *J. Agr. Research* **45**: 627 (1932).
4. Atkeson, F. W., Peterson, W. J., and Aldous, A. E., *J. Dairy Sci.* **20**: 557 (1937).
5. Beck, W. A., and Redman, R., *Plant Physiol.* **15**: 81 (1940).
6. Beeson, K. C., *U. S. Dept. Agr. Misc. Pub.* **369**: 1 (1941).
7. Beeson, K. C., *Soil Sci.* **60**: 9 (1945).
8. Beeson, K. C., *Botan. Rev.* **12**: 424 (1946).
9. Bender, C. B., and Bosshardt, D. K., *J. Dairy Sci.* **22**: 637 (1939).
10. Bennett, E., *Plant Physiol.* **15**: 327 (1940).
11. Bennett, E., *J. Biol. Chem.* **146**: 407 (1942).
12. Bolin, D. W., *J. Agr. Research* **48**: 657 (1934).
13. Bondi, A. H., and Meyer, H., *J. Agr. Sci.* **33**: 123 (1943).
14. Bradley, W. R., Eppson, H. P., and Beath, A. O., *Wyoming Agr. Expt. Sta. Bull.* **241**: 3 (1940).
15. Brink, R. A., and Roberts, W. L., *Science* **86**: 41 (1937).
16. Brunstetter, B. C., Myers, A. T., Wilkins, H. L., and Hein, M. A., *Proc. 6th Summer Conference on Spectroscopy and Its Applications,* pp. 14–19 (1939).
17. Brynmor, T., and Moon, F. E., *Empire J. Exptl. Agr.* **6**: 235 (1938).
18. Burkhart, B. A., *Plant Physiol.* **11**: 421 (1936).
19. Byers, H. G., *U. S. Dept. Agr. Tech. Bull.* **482** (1935).
20. Camburn, O. M., Ellenberger, H. B., Jones, C. H., and Crooks, G. C., *Vermont Agr. Expt. Sta. Bull.* **494**: 3 (1942); *Bull.* **509**: 3–32 (1944).
21. Challinor, S. W., Haworth, W. N., and Hirst, E. L., *J. Chem. Soc.* 1560 (1934).
22. Chibnall, A. C., "Protein Metabolism in the Plant." 306 pp. New Haven (1939).
23. Clarke, I. D., Frey, R. W., and Hyland, H. L., *J. Agr. Research* **58**: 131 (1939).
24. Coop, I. E., *New Zealand J. Sci. Tech.* **22B**: 71 (1940).
25. Couch, J. F., *J. Chem. Ed.* **14**: 16 (1937).
26. de Cugnac, *Ann. Sci. Nat.* **13**: 1 (1931).
27. Eheart, J. F., and Pratt, A. D., *Virginia Agr. Expt. Sta. Tech. Bull.* **81**: 3 (1942).
28. Ellenberger, H. B., Newlander, J. A., and Jones, C. H., *Vermont Agr. Expt. Sta. Bull.* **295**: 3 (1929).
29. Fernholz, E., and Moore, M. L., *J. Am. Chem. Soc.* **61**: 2467 (1939).
30. Forbes, E. B., and Keith, M. H., *Ohio Agr. Expt. Sta., Tech. Series Bull.* **5** (1914).
31. Foreman, F. W., *J. Agr. Sci.* **28**: 135 (1938).
32. Franzke, C. J., Puhr, L. F., and Hume, A. N., *South Dakota Agr. Expt. Sta. Tech. Bull.* **1** (1939).
33. Fraps, G. S., and Rather, J. B., *Texas Agr. Expt. Sta. Bull.* **150** (1912).
34. Graber, L. F., Nelson, N. T., Leukel, W. A., and Albert, W. B., *Wisconsin Agr. Expt. Sta. Research Bull.* **80** (1927).
35. Grandfield, C. O., *J. Agr. Research* **67**: 33 (1943).
36. Greenhill, A. W., *Biochem. J.* **30**: 412 (1936).
37. Hale E. B., Davis, G. K., and Baldwin, H. R., *J. Biol. Chem.* **146**: 565 (1942).
38. Hauge, S. M., *J. Biol. Chem.* **108**: 331 (1935).
39. Haworth, W. N., Hirst, E. L., and Lyne, R. R., *Biochem. J.* **31**: 786 (1937).
40. Hodgson, R. E., Knott, J. C., Graves, R. R., and Murer, H. K., *J. Agr. Research* **50**: 149 (1935).

41. Huffman, C. F., *J. Dairy Sci.* **22**: 889 (1939).
42. Hunt, C. H., and Bethke, R. M., *J. Nutrition* **20**: 175 (1940).
43. Ingalls, R. A., and Shive, J. W., *Plant Physiol.* **6**: 103 (1931).
44. Jaretzky, R., *Angew. Botan.* **22**: 147 (1940).
45. Johnson, I. J., and Miller, E. S., *J. Am. Soc. Agron.* **32**: 302 (1940).
46. Kemmerer, A. R., Fudge, J. F., and Fraps, G. S., *J. Am. Soc. Agron.* **36**: 683 (1944).
47. Kohler, G. O., *J. Biol. Chem.* **152**: 215 (1944).
48. Kon, S. K., and Thompson, S. Y., *J. Agr. Research* **30**: 622 (1940).
49. Léeman, A. C., *Onderstepoort J. Vet. Sci. Animal Ind.* **5**: 97 (1935).
50. Louw, J. G., *Onderstepoort J. Vet. Sci. Animal Ind.* **17**: 165 (1941).
51. Lugg, J. W. H., *Biochem. J.* **33**: 110 (1939); **38**: 408 (1944).
52. Lugg, J. W. H., *J. Council Sci. Ind. Research* **14**: 209 (1941).
53. McElroy, L. W., and Goss, H., *J. Biol. Chem.* **130**: 437 (1939).
54. Macy, P., *Plant Physiology* **11**: 749 (1936).
55. Man, Th. J. de., *Naturwissenschaften* **31**: 492 (1943).
56. Melville, J., and Doak, B. W., *New Zealand J. Sci. Tech.* **22B**: 67 (1940).
57. Miller, E. C., "Plant Physiology." 2nd ed., 1201 pp. New York (1938).
58. Mitchell, H. H., and McClure, F. J., *Nat. Res. Council Bull.* **99** (1937).
59. Moon, F. E., *Empire J. Exptl. Agr.* **7**: 225, 235 (1939).
60. Morgal, P. W., Petering, H. G., and Miller, E. J., *Ind. Eng. Chem.* **33**: 1298 (1941).
61. Morrison, F. B., "Feeds and Feeding." 20th ed., 1050 pp. Ithaca, New York (1945).
62. Newlander, J. A., and Jones, C. H., *Vermont Agr. Expt. Sta. Bull.* **348** (1932).
63. Newlander, J. A., Jones, C. H., and Ellenberger, H. B., *Vermont Agr. Expt. Sta. Bull.* **362** (1933).
64. Norman, A. G., *J. Agr. Sci.* **25**: 529 (1935).
65. Norman, A. G., *Biochem. J.* **30**: 1354 (1936); **33**: 1201 (1939).
66. Norman, A. G., "The Biochemistry of Cellulose, in Polyuronides, Lignin, etc." 232 pp. Oxford (1937).
67. Norman, A. G., and Richardson, H. L., *Biochem. J.* **31**: 1556 (1937).
68. Norman, A. G., Wilsie, C. P., and Gaessler, W. G., *Iowa State College J. Sci.* **15**: 201 (1941).
69. Orr, J. B., "Minerals in Pastures and Their Relation to Animal Nutrition." 150 pp. London (1929).
70. Osborne, T. B., "The Vegetable Proteins." 151 pp. London (1924).
71. Pagé, E., and Maynard, L. A., *Ind. Eng. Chem.*, **32**: 1140 (1940).
72. Painter, E. P., *North Dakota Agr. Expt. Sta. Bimonthly Bull.* **5**: 20 (1943).
73. Peterson, W. H., Hastings, E. G., and Fred, E. B., *Wisconsin Agr. Expt. Sta. Research Bull.* **61** (1925).
74. Phillips, M., and Davis, B. L., *J. Agr. Research* **60**: 775 (1940).
75. Phillips, T. G., Smith, T. O., and Harper, R. H., *New Hampshire Agr. Expt. Sta. Tech. Bull.* **81** (1943).
76. Pollard, A., *Biochem. J.* **30**: 382 (1936).
77. Pollard, A., Chibnall, A. C., and Piper, S. H., *Biochem. J.* **25**: 2111 (1931).
78. Rewald, B., *Oil and Soap* **21**: 50 (1944).
79. Russell, F. C., *Imp. Bur. Animal Nutrition Tech. Com.* **15**: 7 (1944).
80. Schneider, B. H., "Feeds of the World, Their Digestibility and Composition." 299 pp. Charleston, W. Va. (1947).
81. Seshan, P. A., and Sen, K. C., *J. Agr. Sci.* **32**: 202 (1942).

82. Shorland, F. B., *Nature* **153**: 168 (1944).
83. Smith, A. M., and Wang, T., *J. Agr. Sci.* **31**: 370 (1941).
84. Smith, J. A. B., and Chibnall, A. C., *Biochem. J.* **26**: 218, 1354 (1932).
85. Snider, H. J., *Soil Sci.* **56**: 187 (1943).
86. Snider, H. J., *Illinois Agr. Expt. Sta. Bull.* **518** (1946).
87. Stone, R. W., Bechdel, S. I., McAuliffe, H. D., and Malzahn, R. C., *Pennsylvania Agr. Expt. Sta. Bull.* **444** (1943).
88. Sullivan, J. T., and Garber, R. J., *Pennsylvania Agr. Expt. Sta. Bull.* **489** (1947).
89. Symposium on the nitrogen-free extract of foods and feeding stuffs. *J. Assoc. Official Agr. Chem.* **23**: 102 (1940).
90. Watson, S. J., "Science and Practice of Conservation; Grass and Forage Crops." 403 pp. London (1939).
91. Watson, S. J., and Ferguson, W. S., *J. Agr. Sci.* **22**: 235 (1932).
92. Weinmann, H., *J. So. African Botany* **10**: 37 (1944).
93. Weinmann, H., and Reinhold, L., *J. So. African Botany* **12**: 57 (1946).
94. Whitehead, E. I., and Olsen, O. E., *Proc. South Dakota Acad. Sci.* **21**: 67 (1941).
95. Wilson, J. K., *J. Am. Soc. Agron.* **35**: 279 (1943).
96. Wiseman, H. G., Kane, E. A., Shinn, L. A., and Cary, C. A., *J. Agr. Research* **57**: 635 (1938).
97. Vickery, H. B., *J. Biol. Chem.* **65**: 81, 657 (1925).
98. Vickery, H. B., *Physiol. Rev.* **25**: 347 (1945).
99. Virtanen, A. I., Hausen, S. V., and Saastamoinen, S., *Biochem. Z.* **267**: 179 (1933).
100. Virtanen, A. I., *Nature* **137**: 237 (1936).

Chapter IV

THE CHEMISTRY OF MEAT AND MEAT PRODUCTS

R. C. Miller

The Pennsylvania State College, State College, Pa.

Meats make an important contribution to the diet as excellent sources of protein, fatty acids, and certain minerals and vitamins. In addition meat has an intrinsic value as one of the most satisfying of all foods. In general, the term meat is very inclusive. Fresh meats include primarily the flesh of beef, pork, lamb, veal, mutton, and poultry together with certain edible organs and tissues such as the liver, heart, and kidney. Cured meats such as ham and bacon are prepared by the application of salt and other curing materials together with smoke and have been used for many years. More recently there has been a growing consumption of processed meat products which may be derived from a variety of animal tissues or organs. A new development in the meat industry is the preservation by frozen storage of cuts of meat heretofore offered to the consumer in the fresh stage.

Most of the fresh meat commonly consumed consists of muscle meats derived from the voluntary muscles which consist of muscle fibers bound together with connective tissue. The muscle meat of the involuntary muscles such as the heart and the walls of the gastrointestinal tract is of the smooth or nonstriated type. Muscle fibers consist of tubular shaped fibriles which are imbedded in sarcoplasm, a framework of connective tissue being distributed throughout the muscle fibers. The proportionate amount of connective tissue determines, to a degree, the tenderness of the meat.

The Composition and Nutritive Value of Meat

The composition of meat is dependent on a number of factors including the relative proportions of lean and fatty tissue, the type of animal, and its stage of development. Furthermore, meat from different species differs somewhat in composition as also do cuts from the same animal. Different grades of meat also differ to some extent, the higher quality meats having the greatest amount of fat.

The water content of meat may vary from 55 to 70 per cent, protein from 15 to 19.5 per cent. Meat may contain fat in amounts up to 35 per cent while the ash or mineral content is approximately 1 per cent or less except in the case of a few meat products.

Proteins and Amino Acids. Muscle contains four proteins: myosin, myogen, globulin X, and myoalbumin. Myosin, a globulin comprising 50 to 70 per cent of the intracellular protein of muscle, has a high degree of hydration which probably accounts, in large part, for the water-holding capacity of muscle tissue. Muscle hemoglobin, a conjugated protein containing iron, may be thought of as the muscle counterpart of blood hemoglobin.

Connective tissue contains somewhat small amounts of elastin and relatively larger amounts of collagen which on hydrolysis is converted into gelatin. There is relatively less collagen in the tissues of young animals. Adipose tissue also contains collagen and elastin.

TABLE 35. AMINO ACID CONTENT OF MEAT (PER CENT IN PROTEIN OF THE MEAT) *

	Beef Muscle %	Pork Muscle %	Lamb Muscle %	Beef Liver %	Pork Liver %	Lamb Liver %
Arginine	6.2	6.4	6.2	5.9	6.1	6.0
Histidine	3.7	3.8	3.1	2.6	2.8	2.7
Isoleucine	5.2	5.1	4.8	4.7	5.2	4.5
Leucine	8.6	8.6	8.5	9.4	9.6	9.0
Lysine	9.1	8.7	8.8	7.4	7.1	7.3
Methionine	2.5	2.4	2.4	2.2	2.2	2.1
Phenylalanine	4.2	4.2	4.3	5.2	5.4	5.6
Threonine	4.5	4.5	4.8	4.3	4.4	4.6
Tryptophan	1.2	1.2	1.2	1.5	1.5	1.4
Valine	5.3	5.5	5.4	6.5	6.4	6.5

* From *Texas Agr. Expt. Sta. Bull.* **708**, 1949.[5]

A variety of inorganic and organic substances may be extracted from meat by water. These, commonly known as extractives, include a number of nitrogeneous substances such as amino acids, creatine, creatinine, inosin, sarcosine, and various purines.

Meat is an excellent source of amino acids and contains liberal amounts of most of the indispensable amino acids.[1, 5, 12, 13] Although all meat proteins do not have the same amino acid pattern there are strikingly similar amounts of each of the individual amino acids in the tissues of beef, pork, and lamb. The amino acid composition of the protein of several meats is given in Table 35.

Whole egg protein is commonly used as a standard in evaluating proteins nutritionally, particularly because this protein is very highly digestible and almost perfectly utilizable by the experimental rats used in conducting such studies. This very high value of whole egg protein is reflected in the excellent pattern of the amino acids that it contains. As compared to whole egg protein beef muscle has been shown to contain amounts of arginine, histidine, and lysine in excess of the amounts of these amino acids found in whole egg. The other amino acids of beef muscle are present in smaller amounts than they are in egg protein and, of these, cystine and methionine are indicated as being the limiting amino acids of beef muscle.[11]

Studies of the growth and maintenance of experimental rats have shown that beef muscle protein is somewhat less valuable than egg protein. In comparing the amino acid pattern of these two proteins it is seen that the greatest percentage deficit of amino acids in beef protein, as compared to egg protein, occurs in the case of methionine and cystine; hence, these two amino acids are designated as the limiting amino acids of beef protein.

TABLE 36. CHEMICAL AND BIOLOGICAL RATINGS OF VARIOUS PROTEINS *

Proteins	Chemical Score	Protein Efficiency Ratio	Biological Value	Net Utilization[1]
Egg, whole	100	3.8	96	93
Beef, muscle	71	3.2	76	76
Pork tenderloin	-	3.3	79	79
Beef liver	70	2.7	77	75
Pork, ham, cured	-	2.7	74	74
Beef kidney	65	2.9	77	76
Beef heart	65	3.1	74	74
Gelatin	0	-	25	24

* From data of Block and Mitchell.[1]

[1] $\dfrac{\textit{Biological value} \times \textit{coefficient of true digestibility}}{100}$

Isoleucine is the limiting amino acid of beef liver and of beef heart and tryptophan is the limiting amino acid of gelatin.[11]

The comparative nutritive value of different proteins may be assessed by several methods. "Biological value" (the percentage of absorbed nitrogen that is retained for body purposes) in conjunction with values for digestibility, compares favorably with the "protein efficiency ratio" which is the gain of body weight per unit of protein consumed. The chemical score for a protein is determined as the percentage deficit in the limiting amino acid subtracted from 100. Block and Mitchell[1] have shown that the chemical score has a high degree of correlation with both biological value and protein efficiency ratio as determined with growing rats. In comparing proteins, whole egg protein has been used as a standard since this protein is almost completely utilized by the rat.

Table 36, showing the chemical and biological ratings of meat proteins, is taken from the data of Mitchell and Block [1] and shows the relatively high value of meat proteins as a class. In general meat proteins are almost completely digestible, which enhances their usefulness as dietary components.

Fat. There is a difference in the kind and amount of fat in meat from different species and from different cuts of meat. This may depend in part on the feeding of the animal. Feeding may be reflected also in the "finish" of the animal or carcass. This term is used to denote the amount, color, character, and distribution of the exterior, interior, intermuscular and intramuscular fat and is rather closely related to meat quality.[3]

Fat in meat makes an important contribution to the diet as a source of calories and because of the essential fatty acids it supplies. Furthermore, meat with a good distribution of fat has a highly satiety value. Animal fats are made up largely of oleic, palmitic, stearic, and linoleic acids together with relatively small amounts of arachidonic and linolenic acids. In addition, tissue fat contains the phospholipids, lecithin, cephalin, and sphingomyelin. This type of fat, as compared to storage or depot fat, cannot be detected with the microscope and cannot be extracted with ordinary fat solvents. Storage or depot fat occurs mainly in the subcutaneous connective tissue, the intermuscular connective tissue and the abdominal cavity.

As has been mentioned, the character of the fat carried by an animal is determined in part by its feed. Much of the fat of meat animals is derived from the conversion of food carbohydrates to fat. This type of fat has a relatively low iodine number (55–70) and is firm in character. Contrasted to this is pork fat with a low melting point and higher iodine number such as is produced when pigs are fed softening feeds containing relatively large amounts of fat or oil with higher iodine numbers (65–95) and relatively low melting points. Soybeans and peanuts are feeds of this character, and the pork produced on these feeds is termed soft pork.[9]

Minerals. Inasmuch as meats are derived from active body tissues it might be expected that they would contain many of the mineral elements required by man. This is generally true except for those mineral elements composing the skeleton.[14] Meat is, therefore, a poor source of calcium and is also relatively low in magnesium content. It is, however, a fair source of phosphorus, containing on the average 150–200 mg. of phosphorus per 100 g. Liver and heart contain considerably more phosphorus than does lean muscle meat.

Meats make a major contribution to the human diet because of their relatively high content of iron and copper. Muscle meats contain from 2.5 to 4.0 mg. of iron per 100 g. and liver may contain up to 12 mg. of iron per 100 g. of fresh tissue and is one of the best food sources of iron. Meats are also relatively high in copper content and thus have a high hemopoetic value supplying iron and copper necessary for the regeneration of red blood cells. Other trace mineral elements required in metabolism are found in small amounts in muscle meats and in higher concentrations in liver, notably manganese (15 mg. per kilo) and zinc (80 to 120 mg. per kilo).

Vitamins. Although meats are excellent sources of certain of the vitamins it is not possible to generalize with respect to their vitamin content. Muscle meats contain very little vitamin A or vitamin C and only traces, if any, of vitamin D. Liver, however, is a relatively good source of vitamin A, the amount present depending on the feed of the animal and possibly also its age and species.

TABLE 37. NUTRIENTS SUPPLIED BY 100 GRAM PORTIONS OF VARIOUS MEATS *

Meat	Protein g.	Phosphorus mg.	Iron mg.	Thiamine mg.	Riboflavin mg.	Niacin mg.
Beef, chuck	18.6	200	2.8	0.12	0.15	5.0
Beef, hamburger	16.0	172	2.4	0.10	0.13	4.3
Beef, loin	16.9	182	2.5	0.10	0.13	4.6
Beef, round	19.3	208	2.9	0.12	0.15	5.2
Beef, rump	15.5	167	2.3	0.10	0.12	4.2
Lamb, leg	18.0	194	2.7	0.21	0.26	5.9
Lamb, shoulder	15.6	168	2.3	0.18	0.23	5.2
Lamb, chop	18.0	194	2.7	0.21	0.26	5.9
Pork, bacon	9.1	108	0.8	0.42	0.10	2.1
Pork, ham [fresh]	15.2	164	2.3	0.96	0.19	4.1
Pork, ham [cured]	16.9	182	2.5	0.78	0.19	3.8
Pork, loin	16.4	177	2.5	1.04	0.20	4.4
Pork, picnic	14.8	160	2.2	0.94	0.18	4.0
Pork, sausage	10.8	116	1.6	0.22	0.15	2.3
Veal, chops	19.2	207	2.9	0.18	0.27	6.3
Veal, cutlet	19.5	210	2.9	0.18	0.28	6.4
Veal, leg	19.1	206	2.9	0.17	0.27	6.3
Chicken	20.2	218	1.9	0.11	0.18	8.6
Turkey	20.1	320	3.8	0.12	0.19	7.9
Frankfurters	15.2	164	2.3	0.19	0.23	2.4
Bologna	14.8	160	2.2	0.31	0.30	3.0
Heart	16.5	236	6.2	0.54	0.90	6.8
Liver	19.8	373	12.1	0.27	2.80	16.1
Tongue	16.4	119	6.9	0.22	0.27	5.0

* From tables of Food Composition in terms of Eleven Nutrients. *U. S. Dept. Agr. Misc. Publ. No. 572*, **14.**

With respect to the B-complex, meats are relatively good but somewhat variable sources of these factors.[17] In Table 37 are given the thiamine, riboflavin, and niacin contents of various kinds of meat. It is seen that pork is especially high in thiamine content. This appears to be a species characteristic but is also influenced by the thiamine content of the feed.[10] Most vitamins are found in the largest amounts in the liver but such is not the case for thiamine in pork, the muscle tissue being richest in thiamine in this instance. However, even in lean pork muscle tissue it has been found to be possible to increase the thiamine content by feeding thiamine-rich feeds. The human daily requirement for thiamine may be satisfied with one pork chop. Beef has a much lower thiamine content than pork, while veal and lamb contain slightly larger amounts than beef.

Liver is an excellent source of riboflavin, containing on the average more than ten times as much of this vitamin as the muscle meats. Kidney and heart are also good sources of riboflavin. Meats make a major contribution in satisfying the human dietary requirements for riboflavin and may supply on the average upward of 30 per cent of the human daily requirements for this vitamin.

The major amount of niacin required in the daily diet may also be supplied by meats which are among the best food sources of this factor. Beef and pork contain 4–5 mg. of niacin while veal and lamb contain approximately 6.0 mg. per 100 g. Liver and kidney contain two to three times as much riboflavin as the muscle meats. Bacon is very low in niacin content. The consumption of relatively large amounts of fat pork together with other foods low in niacin content, has been associated with the occurrence of human pellagra especially among people of low economic level.

There are only limited data available to show the content of meat of such factors as pantothenic acid, pyridoxine, choline, biotin, inositol, folic acid, and vitamin B_{12}. However, meats in general are considered to be good dietary sources of these factors, liver probably being the best general source of all of these factors. In addition to the value of liver as a source of the known vitamins it is extremely valuable as a source of those unknown factors which have not yet been identified.

Cooking. Irrespective of its proximate composition the net value of any food is represented by the nutrients contained in the edible portion when fully prepared for consumption. In the cooking of meats some losses of certain nutrients appear to be inevitable. This varies with different nutrients and with different methods of cooking. The largest losses occur when meats are boiled, the amounts of certain vitamins retained being relatively low and the coagulable soluble proteins being extracted from the meat. Thiamine in meat is particularly susceptible to destruction by cooking, whereas riboflavin and niacin losses are usually somewhat less.[2, 6, 7] Smaller losses occur with frying, broiling, and roasting as compared to boiling. The time of cooking is an important factor in determining vitamin losses. It is not believed that cooking causes any serious impairment of the proteins of meats, the net protein value of cooked meats being but slightly less than that of fresh meats.

THE PROCESSING OF MEATS

Aging and Ripening. The Federal Government maintains an inspection service for the certification of the class, quality (grade) and condition of meats in conformity with established standards. Thus meat may be purchased according to standard grades. The average person who purchases meat on the retail market probably has only slight knowledge of the various grades of meat. The acceptability of a particular cut of meat by a consumer probably depends on a number of factors chief among which is appearance. However, the final judgment of the meat will be based on other factors including flavor, juiciness, and tenderness. Tenderness is perhaps the chief attribute of high quality meat in the eyes of the average consumer.

Freshly killed meat, particularly beef, is usually tough. This varies with different muscles, and therefore with different cuts of meat, in relation to their size and function in the body, those which contain less connective tissue being naturally more tender. In practice meat, particularly beef, is made more tender by aging or ripening for periods of from 2 to 6 weeks at temperatures from 36°–40° F. During this aging process tenderness is achieved through the action of proteolytic enzymes, naturally occurring in meat, on the connective tissue constituents, mainly collagen. Two enzymes of plant origin, papain and bromelin, have a similar action and are available for the tendering of individual cuts of meat.

During the ripening or aging of meat the temperature is controlled in such a manner as to permit enzyme action and at the same time minimize bacterial action which might cause spoilage. With beef and lamb carcasses it is highly desirable to have a good fat covering as a further means of protection of lean tissue which might otherwise be exposed to bacteria.

Ultraviolet radiation of meat during ripening may be used as a means of minimizing unflavorable bacterial action, ultraviolet light in the region of 2550 A having a lethal action against most microorganisms.[8] The use of ultraviolet light permits the use of higher holding temperatures during aging, thus the enzyme action is accelerated and effective tendering achieved in from two to three days at approximately 60° F., instead of several weeks at the lower temperatures of 36°–40° F.

Ultraviolet irradiation is undesirable, however, for meats such as pork having exposed fat which is susceptible to the development of rancidity as with skinned pork carcasses.[16]

Curing. The preservation of meat and meat products, particularly pork, by curing with salt, smoke, and other curing agents may be traced back for many centuries. The latest developments are seen in present methods for the curing of ham and bacon.

The curing agents now most frequently employed are salt, saltpeter (potassium nitrate), sodium nitrite, sugar, and hardwood smoke. The purpose of the cure is to preserve the product in a form in which it will keep well and will possess a distinctive flavor, taste, and appeal to the consumer. The immediate objective is to apply the curing agent to the fresh meat as rapidly as is possible before any deterioration takes place. Common salt is the ingredient of the curing mixture which is primarily concerned with preservation action. In most instances the other components of the curing mixture are mixed with the salt.

Two principal methods of applying the cure are by dry curing and by curing with a so-called curing pickle or brine. For the dry-cure the curing agents are applied directly to the surface of the meat by rubbing in successive portions at intervals of two or more days or as rapidly as the meat will absorb it. A satisfactory curing mixture for dry curing is 8 pounds of salt, 3 pounds of sugar, and 3 ounces of saltpeter.[19] In the case of ham and bacon 1 ounce of this mixture is applied per pound of meat. The time of curing will depend on the thickness of the meat and usually seven days per inch of thickness will be required after which time it is ready to be smoked.

Various combinations of salt, sugar and saltpeter dissolved in water may be used for the brine or pickle cure. A suitable mixture is 8 pounds of salt, 3 pounds of sugar, and 3 ounces of saltpeter dissolved in 5 gallons of water, this amount of pickle being sufficient to cure 100 pounds of pork.[19] A pickle containing sugar is known as a sweet pickle. The strength of brine or pickle is measured by a salimeter, one hundred degrees on the salimeter scale representing a concentration equal to that of a saturated solution of salt at 40° F. The 8–3–3 mixture referred to above makes a 75° pickle when dissolved in 5 gallons of water.

There are a number of methods of curing in which a pickle may be used. The simplest is to place the meat in the brine for a specified period which must be long enough to allow the curing ingredients to penetrate to all parts of the meat. The curing process may be speeded up by first injecting pickle into the meat through a needle attached to a syringe or pump, the process being known as pump pickling.[20] This process is used for hams and has the advantage of quickly getting the curing agents into the center of the ham where spoilage is most likely to occur first.

More recently a method has been developed whereby the pickle is introduced into the ham by means of a needle placed in the femoral artery and then the liquid is pumped throughout the system of blood vessels in the ham which are connected to this artery. These methods reduce spoilage in hams and hasten the curing process.

A well-cured product is one in which the curing agent is uniformily distributed. The above methods hasten this process which otherwise requires, under normal conditions, a period of time dependent on the concentration of the curing mixture and the size of the cut being cured.

The function of salt is as a preservative, its main action not being that of a bactericide but simply as an inhibitor of many species of bacteria.[15] Saltpeter is used to give the product its characteristic color, owing to the formation of nitric oxide myohemoglobin and nitric oxide hemoglobin from myohemoglobin and hemoglobin. This conversion occurs through the action of nitrite formed from the saltpeter (potassium nitrate) by nitrate reducing organisms. Since saltpeter is used simply as a potential source of nitrite the latter may replace it in a curing mixture. Sugar is also involved in the formation of the pigments named above, its role, in the presence of microorganisms, being that of the maintenance of the reducing conditions necessary for the pigment formation.[3]

The smoking of cured meats gives them a characteristic flavor and contributes to the preservation of the product through the organic distillates in the smoke. A development of the smoking process in recent years has led to the production of tenderized hams. These are produced by slowly raising the smoke house temperature, usually by stages, until the inside temperature of the ham reaches 140° F. when it is removed. Ready to eat hams are precooked rather than just tenderized, the inside temperature of the ham in this case being held at 155° F. or above, for at least two hours.

RANCIDITY IN MEAT PRODUCTS

With lard and certain other meat products the prevention of the development of rancidity is an important problem.[4] Rancidity develops as the result of the breaking down of fats or fatty acids and is generally classified into two types, either oxidative or enzymatic. Oxidative rancidity develops through the absorption of atmospheric oxygen, whereas enzymatic rancidity results from the splitting of triglycerides into glycerol and free fatty acids by enzyme action. Certain fats are more susceptible to breakdown than others depending in part at least, on their degree of saturation. The undesirable end products of rancidification are peroxides, aldehydes, ketones, and acids of low molecular weight, the aldehydes and ketones probably being responsible for the impairment of flavor, taste, and odor.

Rancidification is accelerated by increases in temperature and exposure to light. Certain metals such as copper and iron, and compounds such as salt and nitrates induce rancidity in certain meat products. Another group of substances retard or delay the onset of rancidity. Among these are certain products isolated from natural oils and termed either antioxidants or synergists, the latter setting up conditions favoring antioxidants rather than acting directly themselves. Many of the antioxidants are di-phenolic compounds with active groups in the ortho or para positions while the synergists are usually acids of the di- or polybasic types. The tocopherols are antioxidants, whereas ascorbic acid is a synergist favoring the action of the tocopherols.

Pork is particularly susceptible to rancidification as compared to beef, veal, or lamb. This fact should be considered when pork is preserved by frozen storage, in many instances the onset of rancidity with frozen pork may occur within two to three months unless the storage temperature is 0° F. or lower. Smoking of pork apparently exerts an antioxidant effect.

There are a large number of compounds and substances that have antioxidant properties. Among these are gum guiac, oat flour, oat oil, N. D. G. A. (nordihydroguaiaretic acid), various tocopherols, gossypol, soybean oil and lecithin cottonseed oil, di-iso-ascorbo palmitate, propyl gallate, and butylated hydroxyanisole. Citric and phosphoric acids are common synergists. The proper use of these substances enhances the value of many animal products.

BIBLIOGRAPHY

1. Block, Richard, and Mitchell, Harold H., *Nutr. Absts. Rev.* **16**: 249 (1946–47).
2. Cover, S., McLaren, B. A., and Pearson, P. B., *J. Nutrition* **27**: 363 (1944).
3. Jensen, L. B., "Microbiology of Meats." Champaign, Illinois, The Gerrard Press (1945).
4. Lea, C. H., "Rancidity in Edible Fats." New York, Chemical Publishing Co., Inc. (1939).
5. Lyman, Carl M., and Kuiken, K. A., *Texas Agr. Expt. Sta. Bull.* **708** (1949).
6. McIntire, J. M., Schweigert, B. S., and Elvehjem, C. A., *J. Nutrition* **26**: 621 (1943).
7. McIntire, J. M., Schweigert, B. S., Henderson, L. M., and Elvehjem, C. A., *J. Nutrition* **25**: 143 (1943).
8. McIntosh, J. A., Sotola, Jerry, Boggs, Mildred, Roberts, June, Prouty, C. C., and Ensminger, M. E., *Wash. Agr. Expt. Sta. Bull.* **422** (1942).
9. Maynard, L. A., "Animal Nutrition." New York and London, McGraw-Hill Book Co., Inc. (1947).
10. Miller, R. C., Pence, J. W., Dutcher, R. A., Ziegler, P. T., and McCarty, M. A., *J. Nutrition* **26**: 261 (1943).
11. Mitchell, H. H., and Block, Richard J., *J. Biol. Chem.* **163**: 599 (1946).
12. Schweigert, B. S., McIntire, J. M., Elvehjem, C. A., and Strong, F. M., *J. Biol. Chem.* **155**: 183 (1944).
13. Schweigert, B. S., Tatman, I. E., and Elvehjem, C. A., *Arch. Biochem.* **6**: 177 (1945).
14. Tables of Food Composition in Terms of 11 Nutrients. *Misc. Publ. No.* **572**, U. S. Dept. Agr. (1945).
15. Janner, F. W., and Evans, F. L., *Zentbl. F. Bakt. Abt.* 11, **88**: 44 (1933).
16. Volz, Frances E., Gortner, Willis A., Pitz, Edward W., Jr., and Miller, John I., *Food Tech.* **3**: 4 (1949).
17. Waisman, Harry A., and Elvehjem, C. A., "The Vitamin Content of Meat." Minneapolis, Minn., Burgess Publishing Co. (1941).
18. Zeigler, P. Thos., "The Meat We Eat." Danville, Illinois, The Interstate Printers and Publishers (1948).
19. Zeigler, P. Thos., and Miller, R. C., *Pa. Agr. Expt. Sta. Bull.* **355** (1938).
20. Zeigler, P. Thos., and Miller, R. C., *Pa. Agr. Expt. Sta. Bull.* **427** (1942).

Chapter V

THE CHEMISTRY OF MILK AND DAIRY PRODUCTS

Arnold H. Johnson

National Dairy Research Laboratories, Inc.
Oakdale, Long Island, N. Y.

The importance of milk in the nutrition of the young has long been recognized. Man knew by observation or learned by experience that the milk of mammals was a good food for himself and his children. This has led to the development of a great industry. In 1948 the total milk production in the United States was 118,337,000,000 pounds. It is from this large quantity of milk that the various products of the dairy industry are produced.

In mammals the food material necessary for starting the young in life is secreted in the mammary glands. The milk thus secreted is of white color and may be creamy to watery in consistency, depending upon the particular mammal from which the milk is obtained. Milk is accordingly a physiological fluid possessing food elements essential to life and characterized by its three main components: fat, lactose, and casein. The inorganic elements necessary to nutrition are present in small, but well-balanced, quantities. The milk also has physical properties adaptable to the digestive tract of the very young. For instance, the casein of the milk is precipitated by the rennin in the infant stomach at low acidities, forming a curd with fat enmeshed in it. Digestion of this curd can then proceed slowly, furnishing a steady supply of fat- and protein-digested products for absorption through the intestine of the young animal.

Composition of Milk. Changes take place in the composition of the milk as the lactation period progresses. The greatest change in milk composition takes place during the first few days after birth of the young. The milk of this period is called the colostrum. The first colostrum of cow's milk is reddish yellow in color and has a strong odor and a bitter flavor. It has a composition of about 27 per cent total solids, 5.08 per cent casein, 11.34 per cent albumin, 1.01 per cent ash, 5.1 per cent fat, and 7.2 per cent lactose. Within five days the milk has become white in color and has the composition of normal cow's milk, as shown in Table 38.

Various important functions have been attributed to the colostrum, among which are the purging of the alimentary tract, coupled with a disinfecting action, and the seeding of the intestines with the proper bacterial flora so that normal milk may be well digested later. Recently it has been shown that the intestinal wall of the calf is permeable to certain proteins of the colostrum, and these proteins impart immunological factors to the young calf. Toward the end of the lactation period there is a decrease in the lactose content of the milk with an increase of the sodium chloride content.

While this discussion will be limited primarily to the chemistry of cow's milk, it may be of interest to set down the composition of the milk of other mammals. In Table 38 the composition of the milk of mammals has been arranged approximately in descending order of degree of development at birth. These data are taken from the compilation of Davies.[23]

TABLE 38. COMPOSITION OF MILK FROM VARIOUS SPECIES OF MAMMALS (PERCENTAGES)

Species	Water	Fat	Sugar	Casein	Other Protein	Ash
Mare	90.68	1.17	5.77	1.27	0.75	0.36
Ass	89.88	1.50	6.09	0.73	1.31	0.49
Mule	91.50	1.59	4.80	1.64		0.38
Camel	86.57	3.07	5.59	4.00		0.77
Llama	86.55	3.15	5.60	3.00	0.90	0.80
Cow	87.32	3.75	4.75	3.00	0.40	0.75
Goat	82.34	7.57	4.96	3.62	0.60	0.84
Buffalo	86.04	4.63	4.22	3.49	0.86	0.76
Reindeer	68.20	17.10	2.08	8.40	2.00	1.50
Sheep	79.46	8.63	4.28	5.23	1.45	0.97
Elephant	67.85	19.57	3.13	3.09		0.65
Pig	84.04	4.55	3.30	7.23		1.05
Cat	81.63	3.33	4.91	3.12	5.96	0.58
Dog	75.44	9.57	3.09	6.10	5.05	0.73
Rabbit	-	16.71	1.98	8.17	2.21	-
Guinea-pig	-	7.31	2.31	4.60	0.49	-
Porpoise	41.11	48.50	1.33	11.19		0.57
Whale	48.67	43.67	-	7.11	-	0.46
Caaing Whale	-	43.76	-	-	-	-
Hippopotamus	-	4.51	-	-	-	-
Human	88.50	3.30	6.80	0.90	0.40	0.20

The use of the milk of animals as food for man dates back to early history. The milk of the sheep, the goat, the horse, the buffalo, the camel, the llama, the reindeer, and the ass have been used for food and at the present time the milk from some of these animals finds use as a food. However, the most widely produced milk is that of the cow and the term "milk" itself is usually taken to mean cow's milk. Milk and the products manufactured from it constitute an important portion of the food supply of nations. Studies on cow's milk have been voluminous and have dealt mainly with composition, technology, nutritive value, analysis, bacteriology, and biochemistry of milk products.

The United States Public Health Service[54] defines milk as "the lacteal secretion, practically free from colostrum, obtained by the complete milking of one or more healthy cows, which contains not less than 8.25 per cent of milk solids-not-fat and not less than 3.25 per cent of milk fat." Because of its function—the nutrition of the young—milk is necessarily a complex product, and its composition shows considerable variation.

Among the factors influencing the composition of milk are breed and individuality of the cow, inheritance, age, physiological state, quality of the food, environment, stage of lactation period, climate, temperature, and season of the year; also intervals between milkings, morning or evening milk, variations during milking, heat of oestrum, excitement, and management of the dairy herd. Davies [23] and Rogers [95] discuss the effects on milk composition of many of these factors, the most important of which is breed, as shown by the data in Table 39. These data indicate variations in the composition of milk and typical analyses of the milk from the important breeds of dairy cows. The first six breeds listed in the table are common in the United States; while the last five, for which complete data are not available, are European breeds of dairy cows. The milk compositions recorded in Table 39 are assembled from data reported by Davies [23] and by Roadhouse and Henderson.[92] It appears, therefore, that the average composition of milk will depend on the breed of cows populating any given dairy section.

TABLE 39. COMPOSITION OF MILK

	No. of Cows from which the tests were averaged	Total Solids %	Moisture %	Fat %	Protein %	Lactose %	Ash %	Specific Gravity %
Minimum		10.56	89.44	2.60	2.44	2.41	0.560	1.0231
Maximum		17.90	82.10	8.37	6.48	6.11	0.956	1.0398
Holstein	37,598	12.26	87.74	3.40	3.32	4.87	0.68	
Shorthorn	6,155	12.81	87.19	3.94	3.32	4.99	0.70	
Ayrshire	6,999	12.90	87.10	4.00	3.58	4.67	0.68	
Brown Swiss	721	13.41	86.49	4.01	3.61	5.04	0.73	
Guernsey	32,562	14.61	85.39	4.96	3.91	4.93	0.74	
Jersey	29,495	14.91	85.09	5.37	3.92	4.93	0.71	
Kerry		13.39	86.61	4.30				
Welsh				4.40				
South Devon		13.27	86.73	4.02				
Lincoln Red		12.76	87.24	3.76				
Red Poll		12.90	87.10	3.81				

A general relationship exists between the fat content of the milk and the solids-not-fat. Thus, a change of 1 per cent in fat content is on the average accompanied by a change of 0.4 per cent in solids-not-fat. However, because of the many factors which affect the fat content of milk, it is not possible to predict the solids-not-fat of milk from the fat content.

Throughout the history of dairying the fat content of milk has been considered to be of prime importance. The market value of milk has, in general, been measured by determining its fat content. Early research was therefore directed to the development of a rapid method that would lend itself to the fast and accurate determination of the fat content of milk. The Babcock method in the United States and the Gerber method in Europe came to be adopted for this purpose. The Babcock method depends on the liberation of fat from the stabilizing protein in the milk by addition of sulfuric acid to the milk, the column of liberated fat being then determined in a special calibrated centrifuge bottle. Details of the process are given in the methods of analysis of the Association of Official Agricultural Chemists.[5] The availability of a method for determining the fat content of milk is one of the milestones in the growth of the dairy industry from many localized enterprises to a great business, handling large quantities of milk.

CHEMISTRY OF THE CONSTITUENTS OF MILK

Fats. Butterfat or milk fat is a triglyceride which differs from other animal and vegetable fat by the high content of the lower fatty acids which it yields on saponification. Hilditch and Thompson[53] have reported the analysis of a sample of milk in accordance with the data given in Table 40.

TABLE 40. PHYSICAL CONSTANTS OF FATTY ACIDS OF BUTTER-FAT

Acids	No. of C Atoms	Molecular Wt.	Melting Point °C.	Boiling Point °C.	Solubility in 100 Ml.				Volatility in Steam
					%	Water	Alcohol	Ether	
Saturated									
Butyric	4	88	-7.0	162 [770 mm.]	3.7	Sol.	Sol.	Sol.	Volatile
Caproic	6	116	-8.0	202-203 [770 mm.]	2.0	0.882 [15°]	Sol.	Sol.	Volatile
Caprylic	8	144	16.5	236-237 [761 mm.]	1.3	0.25 [100°] 0.079 [15°]	Sol.	Sol.	Volatile
Capric	10	172	31.3-.4	268-270 [760 mm.]	2.7	V. sl. sol.	Sol.	Sol.	Volatile
Lauric	12	200	43.6	225 [100 mm.]	4.0	Insol. V. sl. Sol. [100°]	Sol.	Sol.	Appreciably Volatile
Myristic	14	228	54.0	250.5 [100 mm.]	7.9	Insol.	Sol.	Sol.	V. sl. volatile
Palmitic	16	256	63.0	271.5 [100 mm.]	23.8	Insol.	9.9 [20°]	Sol.	Nonvolatile
Stearic	18	284	69.3	291 [100 mm.]	10.7	0.034 [25°]	4.9	17.82 [25°]	Nonvolatile
Arachidic	20	312.3	77.0		0.5				
Unsaturated									
Oleic	18	282	14.0	286 [100 mm.]	38.5	Insol.	14.02 [25°] in 60% alc.	Sol.	Volatile in superheated steam [250° C.]
Linoleic	18	280	-18	230 [16 mm.]	4.7	Insol.	Sol.	Sol.	
Unsaturated	20 22				0.4				

The fatty acid composition given in Table 40 represents a single sample of butterfat. Investigations have shown that the fatty acid content of the butter glycerides is subject to considerable variation. The range of fatty acids in 21 samples of butterfat, as found by Holland[55] and others, is given in Table 41.

TABLE 41. FATTY ACIDS IN 21 SAMPLES OF MILK FAT FROM COWS FED NORMAL RATIONS

Fatty Acid	Acid Content, %	
	Range %	Average %
Butyric	2.4 - 4.23	2.93
Caproic	1.29- 2.40	1.90
Caprylic	0.53- 1.04	0.79
Capric	1.19- 2.01	1.57
Lauric	4.53- 7.69	5.84
Myristic	15.56-22.62	19.78
Oleic	25.27-40.31	31.90
Palmitic	5.78-22.86	15.17
Stearic	7.80-20.37	14.91

Of the various fat constants which may be used in characterizing butter, the Reichert-Meissl and the Polenske values have been the most useful in distinguishing butterfat from other fats. (See Chapter II in Volume I.) The Reichert-Meissl value is a measure of the content of fatty acids in butterfat which are volatile with steam and the Polenske number is a measure of the insoluble volatile fatty acids in butterfat. A tabulation of the constants for butterfat in comparison with constants for some other fats is given in Table 42.

TABLE 42. RANGE OF CONSTANTS FOR BUTTER-FAT AND SOME COMMON OILS AND FATS

	Specific Gravity	Melting Point °C	Solidifying Point °C	Refraction Butyro Scale	Refractive Index	Saponification Number	Iodine Number	Acetyl Number	Reichert-Meissl Number	Polenske Number
Oils	$\frac{15.5^\circ}{15.5^\circ}$			25°	25°					
Olive	0.915-0.918		-6-+10	60-64	1.4659-1.4685	185-196	77-95	10.6	0.6	
Peanut	0.917-0.926		0-+3	65-67.5	1.4691-1.4707	186-196	83-105	9.1	0.5	
Maize	0.921-0.927		-12--10	71-72	1.4729-1.4734	189-194	116-130		0.3-5	
Soy	0.922-0.928		-15--8	71-73	1.4729-1.4742	189-194	121-143		0.4-0.7	
Lard oil	0.915-0.918			54-60	1.4620-1.4660	190-198	67-88		0.2	
Fats	$\frac{100^\circ}{15.5^\circ}$			40°	40°					
Cocoa butter	0.858	28-35	21-27	46-48	1.4566-1.4580	192-202	32-41	2.8	0.2-0.8	
Cocoanut	0.863-0.874	20-28	14-23	33-36	1.4474-1.4495	246-268	8-9.5	0.9-12.3	6.0-8.5	15.5-20.5
Butter	0.865-0.870	28-36	19-24	40.5-46	1.4527-1.4566	220-241	26-38	1.9-8.6	24-34	1.5-3.5
Lard	0.859-0.864	36-46	27-30	48.5-52.5	1.4583-1.4609	193-203	54-70	2.6	0.2-0.8	0.4-0.6

The data in Table 42 show the specificity with which butterfat may be characterized. As stated, the Reichert-Meissl and the Polenske values are most useful, with supporting data being obtained from the melting point and the iodine value. The unsaturated fatty acids in butterfat, oleic and linoleic, are subject to oxidation and allow the development of so-called "oxidized flavor" in dairy products.

In determining the several fat constants listed in Table 42, it is important to follow detailed procedures. These procedures are described by Leach and Winton[69] and in the Methods of Analysis of the Association of Official Agricultural Chemists.[5]

Many factors cause variations in the proportions of the different fatty acids shown in Table 41. Among these factors are feed, plane of nutrition, stage of lactation, season of the year, and breed, among which feed of the cows is the most important factor. Feed concentrates, high in vegetable-oil content, generally increase the oleic acid content of milk fat and decrease the melting point of the fat. Cottonseed oil meal is an exception to the rule in that feeding of this concentrate increases the oleic acid content and decreases the butyric acid content of the milk fat. Underfeeding of the cows usually results in a decline in volatile fatty acids. With regular feeding procedures, the volatile acids of the fat, mainly butyric, decrease and oleic acid increases from the beginning to the end of the lactation period. The fat of milk from Jersey cows is higher in volatile acids than is the milk fat of other dairy breeds. Summer feeding with rich green feeds such as clover tends to produce a soft butterfat of high iodine value. Feeding with winter roughages such as hay and straw have the opposite effect.

Fat-soluble Substances in Milk. Butterfat as obtained from butter contains a variety of fat soluble substances. The yellow color of butter is due to carotene ($C_{40}H_{56}$), which is the precursor of colorless vitamin A (see Chapter XXI in Volume I), also contained in the butterfat. Carotene is converted into vitamin A in the liver by a mechanism which is not well understood. McCollum Orent-Keiles, and Day[71] discuss the several carotenes in relation to vitamin A synthesis. The carotene is derived from green feeds consumed by the cow. Part of the carotene is converted into vitamin A by the cow and part of it is transferred unchanged to the milk. Holstein cows are more efficient in their ability to convert carotene into vitamin A than are Jersey or Guernsey cows, which accounts in part for the yellower color of the milk from the latter two breeds. The considerable variation in green feeds consumed by the cow permits much variation in the carotene or total vitamin A (carotene plus vitamin A) of the milk or butterfat. Dornbush, Peterson, and Olson[27] showed variation of total vitamin A in milk between 1088 and 2415 U.S.P. units per quart.

The fat of milk also acts as a solvent for cholesterol ($C_{27}H_{45}OH$), the milk itself containing this sterol to the extent of about 150 p.p.m.

The fat globules are surrounded by a membrane consisting of a lipid, largely lecithin, and a protein differing in composition from the other milk proteins. Lecithin is a phosphatide, a compound in which one of the fatty acid radicals of the true fatty glyceride is replaced by a choline-phosphoric acid group. Other phosphatides contained in milk are cephalin and sphingomyelin. The total phosphatide content of milk varies between 0.0038 and 0.2889 per cent. The choline of the phosphatides may be a source of trimethylamine, which is responsible for the fishy flavor that develops in dairy products that are not handled properly. Also one or both fatty acid constituents of some of the milk phosphatides are unsaturated and therefore subject to oxidation. Oxidation of these constituents is regarded by some investigators as the source of oxidized flavor development in milk.

Vitamin D is another fat soluble constitutent of milk, but normal milk contains only relatively small quantities of vitamin D (15 International Units per liter). The vitamin D content of milk can, however, be increased substantially by feeding high vitamin D-containing yeast to the cow.

The vitamin E of milk is also contained in the fat, about 0.6 mg. of vitamin E being present in a liter of milk.

Carbohydrates. The lactose content of milk is on the average about 4.8 per cent. Lactose has certain properties which distinguish it nutritionally from other sugars. It is helpful in establishing a slightly acid reaction in the intestine which assists in calcium assimilation. This acidity also operates to prevent the production of gases and mildly toxic substances from protein decomposition. The acid development in the intestinal tract is apparently due to the less rapid hydrolysis and assimilation of lactose, which permits the lactose to persist further along the intestinal tract, thus allowing carbohydrate fermentation with resultant acid production. Lactose is a disaccharide which yields on hydrolysis two aldoses: D-glucose and D-galactose. The hydrolysis of any derivative of lactose gives galactose and the corresponding derivative of glucose, indicating that the aldehyde group of galactose is involved in the disaccharide linkage and the glucose-aldehyde group is free. Whittier [123] has reviewed the structure and configuration of the lactose molecule and the forms and equilibrium in which it exists in solution. The lactose of commerce, $C_{12}H_{22}O_{11} \cdot H_2O$, has the specific optical rotation in water of $(\alpha)^{D}_{20°} = +89.4°$, a melting point of 201.6° C., and is a monohydrate 4-β-D-*galactosyl*-α-D-glucose, being usually designated as the α-lactose hydrate. When α-lactose hydrate is dissolved in water, it exhibits mutarotation from + 89.4° to + 55.5°, the rate of change being a function of temperature, concentration, and the concentration of hydrogen ions and other solutes. Crystallization of lactose below a temperature of 93.5° C. yields the α-lactose hydrate; crystallization above 93.5° yields the 4-β-D-galactosyl-β-D-glucose, usually known as β-lactose anhydride or β-lactose. When pure β-lactose is dissolved in water, it has an initial rotation of + 35° which, on mutarotation, attains the equilibrium value of + 55.5°. A solution of lactose in equilibrium at 25° C. has 62.25 per cent of its lactose in the β-form and 37.75 per cent in the α-form. The initial solubilities of α- and β-lactose show wide differences: at 0° C. 5 g. of α-lactose dissolve in 100 g. of water and 45.1 g. of β-lactose in 100 g. of water. However, when equilibrium between α- and β-lactose is attained, the final solubility will be the same regardless of whether α- or β-lactose was originally added to the water. The commercial preparation of lactose from milk is described on page 151.

Glucose may be present in very small amounts in normal milk. Whitnah [125] found indications from 0 to 0.35 per cent of glucose in milk. Polonovski and Lespagnol [83] report the finding of two new sugars, as well as a gluco-protein in human milk. The sugars are indicated as gynolactose and allolactose. Gynolactose yields glucose and galactose on hydrolysis, has a melting point of 165° C., and a rotation $(\alpha)_D + 20°$.

Proteins. Milk contains three principal proteins: casein (3 per cent), lactalbumin (0.5 per cent), and lactoglobulin (0.05 per cent). Casein is a phosphoprotein; that is, a phosphoric radical enters into its chemical structure. The ease of preparation of casein by precipitating it from skim milk at its isoelectric point (pH 4.6) enables casein to be isolated in pure form in large quantity.

After removal of the casein from the milk, there remains in the whey the two water soluble proteins: lactalbumin and lactoglobulin. Lactalbumin may be prepared directly from milk by saturation of the milk with $MgSO_4$, filtering and then acidifying the filtrate by the gradual addition of 0.25 per cent acetic acid until the filtrate becomes permanently turbid. The precipitate which forms on standing is the lactalbumin, which may be further purified by dissolving in saturated $MgSO_4$ solution and re-acidifying. Lactoglobulin may also be prepared directly from milk by first precipitating the casein from the milk by saturating with NaCl, filtering, and then saturating with $MgSO_4$. The precipitate which forms is the lactoglobulin. These water-soluble proteins may be precipitated simultaneously from whey by heating to temperatures of 185° F. and above.

After removal of casein, albumin, and globulin of milk, there still remains 0.02 to 0.03% of nitrogen in solution. This small quantity of nitrogen is due to the presence of traces of urea, ammonia, creatin, uric acid, creatinin, peptides, and amino acids.

The proteins of milk are of excellent quality due to the nutritional completeness of their amino acid composition and because of their ability to supplement other proteins that may be lacking in one or more of the essential amino acids. Amino acid composition of milk and milk proteins is given in Table 43.

Casein in a white tasteless, odorless, noncrystalline solid usually containing 7 to 8 per cent of moisture. It gives all the protein color reactions, viz., the biuret, Millons; xanthoproteic, Hopkins and Cole and Neubauer-Rhode. Moist casein is soluble in dilute solutions of mineral and organic acids, but the dry casein is less soluble. The concentration of acid necessary to bring about rapid and maximum solution is about 0.01 normal.

Linderstrøm-Lang [70] showed that casein was not a completely homogeneous protein. More recently, Warner [117] has separated casein by electrophoretic methods into two fractions indicated as α- and β-casein. These fractions were shown to be completely separated from each other but were nevertheless not homogeneous. According to Gordon, Semmett and Morris [38] α-casein makes up about 69 per cent and β-casein about 31 per cent of the total. Chemical differences between the two caseins were found by these latter workers.

Casein finds many industrial uses, as a sizing or a binding agent in paper making, as a constituent of casein paints, as an adhesive, as a plastic, for synthetic fibers and textiles, as an emulsifying agent, for the preparation of hydrolysates and for many pharmaceutical products.

Acid precipitated casein is satisfactory for most of these uses but rennin precipitated casein is usually preferred for the manufacture of plastics. Sutermeister and Browne[111] discuss the manufacture and industrial uses of casein. Details of the commercial separation are given in page 151.[70]

Lactalbumin and lactoglobulin have not been prepared for industrial purposes, but mixtures of these proteins isolated by heating whey have been used as special dietary protein and for preparing protein hydrolysate.

Table 43. Composition of Milk Proteins

	Milk Protein %	Casein %	Lacto-Globulin %	Lactalbumin %
Carbon		52.96	52.88	52.51
Hydrogen		7.05	6.96	7.10
Nitrogen		15.85	15.44	15.43
Phosphorous		0.85	0.24	trace
Sulphur		0.72	0.86	1.92
Oxygen		22.77	24.64	23.04
Total		100.20	101.02	100.00
Leucine	8.50	9.8	15.4	9.9
Isoleucine	5.68	5.6	8.4	6.2
Valine	6.71	6.7	5.8	6.0
Phenylalanine	4.50	5.8	3.5	3.6
Arginine	3.09	3.9	2.9	3.5
Histidine	2.68	3.0	1.6	1.9
Threonine	4.78	4.5	5.1	5.1
Methionine	2.28	3.1	3.2	2.8
Lysine	7.36	7.6	11.4	10.9
Alanine	-	3.2	6.2	2.4
Aspartic acid	-	7.2	11.4	10.9
Cystine	-	0.4	3.4	3.1
Proline	-	10.6	4.1	6.0
Serine	-	5.9	5.0	4.9
Tryptophan	-	1.2	1.9	1.9
Tyrosine	-	6.1	3.8	3.9
Glutamic acid	-	21.7	19.5	15.6
Glycine	-	2.7	1.4	0.4
Total[1]	-	109.00	114.00	99.00

[1] The total weight of the amino acids should come to 115–120% due to the introduction of water of hydrolysis.

Hansen and Phillips[47] have studied the relation of time of ingestion of colostrum to the level and distribution of blood serum proteins in the newborn calf. Electrophoretic studies of the blood serum of calves fed colostrum within 24 hours after parturition showed a substantial proportion of the protein to be similar to the proteins of colostrum, while for calves fed colostrum after 24 hours or fed no colostrum at all the electrophoretic pattern of the blood serum indicated only very small quantities of these globulins. The similarity of the globulins of colostrum and normal milk is, however, indicated by immunological tests.

Flanigan and Supplee[32] describe the manufacture of a soluble lactalbumin. Whey substantially free from casein and fat is brought to pH

4.35–4.85 by the addition of hydrochloric and then heated to above 160° F. The albumin is precipitated by this procedure and may be removed by passing the whey through a filter press. The press cake is then dissolved by the addition of alkali. After complete solution of the lactalbumin the solution is brought to pH 6.9 with hydrochloric acid, and the product is then spray-dried to yield a soluble lactalbumin.

Inorganic Constituents. The mineral constituents or the ash content of milk averages about 0.75 per cent with a variation of 0.60 to 0.80 per cent depending on conditions of milk production, seasonal variation, individuality of the producing animals, stage of lactation, feed, and other factors. Because of the importance of the milk minerals, many investigators have determined the inorganic constituents in milk. Table 44 gives the results of some of these investigations which were assembled by Davies.[23]

TABLE 44. COMPOSITION OF THE ASH OF COW'S MILK

	Richmond[90]	Babcock[7]	Fleischmann[33]	Schrodt[100] and Hansen	Orla-Jensen[77] [Average]	Storch[107]
Ash %	0.75	0.72			0.72-0.77	
P_2O_5 % of Ash	29.33	24.29	21.57	24.11	26.89	28.69
CaO % of Ash	20.27	20.01	24.68	21.45	27.32	21.93
MgO % of Ash	2.80	2.42	3.12	2.54	2.42	2.87
Cl % of Ash	14.00	14.28	16.38	14.60	13.57	13.73
SO_3 % of Ash	Trace	3.84	-	4.11	2.96	-
Fe_2O_3 % of Ash	0.40	0.13	0.31	0.11	-	-
Na_2O % of Ash	6.67	10.01	11.92	10.94	5.82	9.44
K_2O % of Ash	28.71	25.02	25.71	25.42	23.63	25.31

The calcium and phosphorus contents of milk are of special importance in nutrition because milk is such an important dietary source of these elements. Attempts to change the mineral constituents of milk by feeding have not yielded definite results. Thus increasing the calcium, copper, or the iron content of the feed has not changed significantly the contents of these minerals in the milk.

In addition to the ash elements given in Table 44 milk contains small quantities of many other minerals such as copper, cobalt, iron, zinc, iodine, manganese, boron, lead, tin, titanium, vanadium, rubidium, silicon, strontium, chromium, barium, germanium, and others. Considerable study has been made of the iron and copper contents of milk because of their nutritional and organoleptic significance. Milk contains about 0.15 p.p.m. of copper and 2.5 p.p.m. of iron.

Milk freshly drawn from the cow has an acidity equivalent to pH 6.6–6.8 and a titratable acidity (phenolphthalein end point) expressed as lactic acid of 0.12 to 0.15 per cent. The latter may vary between 0.10 to 0.25 per cent.

Lactic acid is present only in traces, if at all in freshly drawn milk. Rice and Markley [89] attribute the apparent acidity of milk to the following constituents:

Acidity due to carbon dioxide	0.01 to 0.02%
Acidity due to citrates	0.01%
Acidity due to casein	0.05 to 0.08%
Acidity due to other milk proteins less than	0.01%
Acidity due to phosphates	remainder

Gases contained in freshly drawn milk are carbon dioxide, oxygen, and nitrogen. Freshly drawn milk is very low in oxygen but contains a considerable quantity of carbon dioxide. On exposure to the air, nitrogen and oxygen are dissolved in the milk in accordance with the partial pressures of these gases in the air. Pasteurization or other heat treatment removes dissolved gases from the milk but unless precautions are taken the milk is reaerated on cooling. Noll and Supplee [74] found that mixed raw milk as received at a commercial milk plant over a period of several months averaged 0.47 volume per cent oxygen, 1.29 volume per cent nitrogen and 4.45 volume per cent carbon dioxide.

Citric acid is a usual but variable constituent in milk. Results of a number of investigations show the citric acid content of individual milks to vary between 0.07 and 0.40%. This variation does not appear to be due to breed differences, period of lactation, or feed. Supplee and Bellas[110] report much variation in the citric acid content of milk due to individuality of the cows. The citric acid content of milk is of significance in connection with the formation of calcium citrate crystals in stored evaporated milk and in connection with its function of forming diacetyl ($CH_3COCOCH_3$) and acetylmethylcarbinol ($CH_3COCHOHCH_3$) by the action of certain starters in the production of cultured dairy products.

Vitamins. As a material provided by nature primarily as a food, milk may be expected to contain the various food elements as they are discovered. This has been particularly true of the vitamins. In Table 45, the vitamin content of cow's milk is given. The total vitamin A content of milk consisting of true vitamin A and carotene, the precursor of vitamin A, varies widely due primarily to the feed of the cows. When the cow consumes an abundance of green grass or silage or high-quality green hay, the total vitamin A content of the milk will be high, while feeding procedures not providing carotene-rich materials result in producing milks low in vitamin A.

Milk is not usually considered a good source of vitamin C (ascorbic acid): substantial proportions of this vitamin are lost in handling and processing the milk due to oxidation processes. Knight, Dutcher and Guerrant [65] found the ascorbic acid content of freshly drawn milk to be about 20 mg. per liter. Feeding 100-g. quantities of ascorbic acid did not increase the ascorbic acid content of milk, but the intravenous injection of 24 g. of the compound for 3 successive days increased the ascorbic acid content of the milk from 20 to 30 mg. per liter. Hand[46] discusses the changes in ascorbic acid that take place in the handling and processing of milk and suggests a means of preventing the destruction of the vitamins by deaerating the milk.

TABLE 45. TYPICAL VITAMIN CONTENT OF COW'S MILK

Vitamins	Amount per Liter
A	1,600 to 3,000 I.U.
D	15 I.U.
	430 I.U. [Vitamin D milk]
Thiamine	0.41 mg.
Riboflavin	1.72 mg.
Pyridoxine	0.67 mg.
Pantothenic Acid	3.30 mg.
p-amino benzoic acid	0.15 mg.
Niacin	0.82 mg.
Choline	185.00 mg.
C	8.2 mg.
Biotin	28.0 gamma
Inosital	0.18 mg.
Folic acid	50.0 gamma
E	0.6 mg.

The vitamin D content of the milk is relatively low and does not show significant variations on the feeds normally available to dairy cattle. However, the content of this vitamin in the milk can be increased substantially by feeding irradiated yeast or other material high in vitamin D.

The content of the several B vitamins in cow's milk shows some variation as a result of feeding, season, geographical location, and period of lactation, but the variations are relatively small and no generalization can be made. The vitamin content and food value of various dairy products is well summarized in a recent publication.[84]

Miscellaneous Constituents of Milk. Milk contains various enzymes which are often important in certain processing steps. The functioning of the enzyme will be discussed in connection with the processing step involved. It is sufficient to state here that milk contains the following enzymes: protease (sometimes called galactase), diastase, phosphatase, lipase, catalase, peroxidase, reductase, aldehydase (Shardinger's enzyme), and perhaps lactase. The lipase activity of milk may be responsible for fat hydrolysis in milk produced late in the lactation period. In these milks lipase activity is greater than in milks produced earlier in the lactation period. Bitter and rancid flavors are produced in milk or cream in which the fat has undergone lipolytic splitting.

The flavor of milk is due to the combination of sweetness from the lactose, the nuttiness from the milk fat and the proteins and the saltiness from the milk minerals. Protein and fat also give body to the flavor.

Milk may absorb flavors from the environment or flavors may be imparted to milk from the feed of the cows. Milk heated to high temperatures may contain hydrogen sulfide originating from the lactalbumin.

Physical Properties of Milk. The white opaque color of milk is due to the scattering of reflected light by colloidally dispersed fat, protein, and calcium phosphate. The yellow color of milk or cream is due to the carotene contained in the milk fat. Butter is yellow due to concentration of the carotene-containing fat. The riboflavin in milk introduces a yellowish green color which is intensified in the whey obtained in cheese making or on removing fat and casein curd from milk.

Milk of normal composition has an average specific gravity of about 1.032. Since the fat of milk has a specific gravity of 0.93, the specific gravity of the various dairy products varies with the fat content. Skim milk has a specific gravity of 1.035 and cream of 40 per cent fat has a specific gravity of 0.993.

The freezing point and boiling point of milk are respectively lower and higher than those for pure water because of sugar and salts dissolved in the milk. The freezing point for normal milk is -0.54 to $-0.55°$ C. and the boiling point is 100.17° C. Because of the constancy of these values they may be used in detecting abnormal and "watered" milk. The lowering of the freezing point has been used most frequently for this purpose and an apparatus known as the Hortvet cryoscope has been devised for accurately measuring the freezing point of milk.

The electrical conductivity and the refractive index are also characteristic constants for milk. The electrical conductivity of normal milk is 45 to 48×10^{-4} mho, and variations outside this range may indicate addition of water to milk or milk from diseased udders. The refractive index of milk is usually determined by use of the dipping refractometer on a clear whey prepared from the milk. Values obtained for such wheys vary between 37 and 39. It is claimed that addition of 5 per cent of water can be detected by determination of the refractive index.

Specific heat of milk and milk products is often necessary in calculating heat and refrigeration requirements. The specific heats for whey, skim milk, whole milk, and butterfat are 0.978, 0.940, 0.920, and 0.445, respectively.

MARKET MILK

Milk production for the United States was 121,891,000,000 pounds in 1947. The fluid or market milk industry utilized 57,295,350,000 pounds of this supply as fluid milk or cream. The remainder was used for such products as butter, cheese, evaporated and concentrated milks, dried milks, and other dairy by-products.

Milk from inspected and approved farms is delivered to milk receiving stations where the milk from each producer is inspected for quality in accordance with a definite program. This program involves daily inspection of the incoming milk for temperature and odor, and periodic tests for sediment, bacterial content and acidity if indicated. Samples are taken daily for inclusion in the composite sample for butterfat analysis. Bacterial standards and other details important in sanitary milk production and milk processing as well as the several grades of milk defined by the bacterial standards have been described in Public Health Bulletin 220 of the United States Public Health Service.[84] These grades and their associated bacterial contents are shown in Table 46.

TABLE 46. GRADES OF MILK AND THEIR ASSOCIATED BACTERIAL CONTENTS

Certified Raw Milk	Logarithmic Average Bacterial Plate Count per Cubic Centimeter	Arithmetic Reduction Time[1] in Hours
Grade A raw	0 to 50,000	At least 8
Grade B raw	51,000 to 200,000	6 to 8
Grade C raw	210,000 to 1,000,000	3 1/2 to 6
Grade D raw	over 1,000,000	Less than 3 1/2
A pasteurized	0 to 30,000	
B pasteurized	0 to 50,000	
C pasteurized	Over 50,000	

[1] Methylene blue.

The development of the Babcock test for the rapid determining of the fat content of milk provided a basis for the prompt evaluation of milk and was one of the factors which operated to change the dairy business from many localized enterprises to the large industry that is today with specialized functions of production, transportation, processing, and distribution.

Milk Processing. *Pasteurization.* Another fact which has helped create a great commercial dairy industry is the wide adoption of pasteurization. This process as applied to market milk involves the heating and holding the milk at an elevated temperature, followed by cooling. The conditions of heating must be such that pathogenic bacteria are destroyed, and in most localities pasteurization procedures are defined and enforced by the health authorities. The United States Public Health Ordinance defines pasteurization and similar terms "to refer to the process of heating every particle of milk or milk products to at least 143° F. and holding at such temperature for at least 30 minutes or to at least 160° F. and holding at such temperature for at least 15 seconds, in approved, properly operated equipment: *provided,* that nothing contained in this definition shall be construed as disbarring any other process which has been demonstrated to be equally efficient and is approved by the State Health Authority." The two types of pasteurization defined in the ordinance are usually described as the holding method and the high temperature, short-time method. Details of methods of conducting milk pasteurization are given by Roadhouse and Henderson.[92]

The efficiency of pasteurization may be determined by the so-called phosphatase test. Milk contains the enzyme, phosphatase, which is inactivated under proper pasteurizing conditions. If the milk has not had sufficient heat treatment or if raw milk is present in milk thought to be pasteurized, phosphatase activity in such milk may be demonstrated by the liberation of phenol from phenyl phosphoric ester by the action of phosphatase. The liberated phenol may then be determined by a colorimetric procedure. Other enzymes of milk, including amylase and diastase, have have been used to test the effectiveness of pasteurization.

There has, of course, been much interest in the possible effects of pasteurization on the nutritive properties of milk. In reviewing this problem to 1916 Lane-Claypon[68] concludes that there is little if any impairment of nutritive value by heating milk to boiling point or below. Since 1916, studies on the pasteurization of milk have dealt largely with the effects on the several vitamins. For those vitamins on which data are available (except vitamin C) the vitamin content does not appear to be affected significantly by pasteurization. In the case of vitamin C, heating in the presence of oxygen destroys this vitamin, but, since milk is not depended upon as a source of vitamin C, its loss is not nutritionally important. The holding method of pasteurization causes greater destruction of vitamin C than does the high-temperature, short-time method.

The function of ascorbic acid in the development of oxidized flavor has been studied by Greenbank[40] who suggested that the flavor is the result of an intermediate oxidation product and that the development of the oxidized flavor may be inhibited by reducing or oxidizing agents. Krukovsky, and Guthrie[66] were able to prevent the development of oxidized flavor in milk by rapidly oxidizing the ascorbic acid with hydrogen peroxide. The same milk was made susceptible to the development of oxidized flavor by the addition of ascorbic acid. The presence of copper catalyzed the development of oxidized flavor in the presence of ascorbic acid. Greenbank[41] has presented an excellent review of oxidized flavor in milk and milk products.

The effect of heat and in particular the effect of pasteurization on the denaturation of lactalbumin and lactoglobulin of milk has been the subject of much study. The most recent critical study was by Rowland[97] who found that about 10 per cent of the albumins and globulins were denatured on heating the milk for 30 minutes at 63 to 65° C. (145.2 to 150° F.). On holding milk at 70° C. (158° F.) for 2.5 minutes about 8 per cent of the albumin and globulin of milk was denatured. These temperature conditions are as close to pasteurization conditions as can be selected from the data of Rowland. Rowland, and Harland and Ashworth[48] have found the whey protein nitrogen in milk to be characteristic for normal milk. Rowland interpreted high whey protein nitrogen to indicate abnormal milk from diseased udders. Harland and Ashworth[48] have used whey protein nitrogen as a means of determining whether milk had been heated sufficiently to impart satisfactory baking quality to it.

In determining the effect of pasteurization on calcium and phosphate compounds of milk, Bell[9] has confirmed earlier work that pasteurization causes no significant change in the solubility of these compounds.

The fat of milk is not affected chemically by pasteurization temperatures. Pasteurization may, by a physical effect on the fat globules, cause a change in the manner of separation of the cream layer, however. In order that milk have a cream volume comparable with that of the raw milk, it is important that specified pasteurization temperatures not be exceeded.

Homogenization. Another treatment imparted to a substantial proportion of the fluid milk supply is that of homogenization. The principal effect of homogenization is to reduce the size of the flat globules from a normal diameter of 4 to 8 microns to less than 2 microns.

Homogenization is usually accomplished by passing milk under high pressure through small apertures in equipment known as homogenizers or viscolizers. Recently two other devices have been used to subdivide the fat globules, one using supersonic energy, the other low pressure rotary homogenizers. This process increases the fat surface about 30 times and renders the fat more susceptible to lipolytic hydrolysis. Consequently homogenization is accompanied by sufficient heat treatment to inactivate the lipase of milk. The usual procedure is to heat the milk to 140° F. in order to melt the fat and partially inactivate the lipase. Homogenization at proper pressure for the type of equipment used is then carried out, the milk is clarified, pasteurized at once in order to complete the inactivation of the lipase, cooled, and bottled. Homogenized milk is defined[84] as "milk which has been treated in such manner as to insure break-up of the fat globules to such an extent that after 48 hours storage no visible cream separation occurs on the milk and the fat percentage of the top 100 ml. of milk in a quart bottle, or of proportionate volumes in containers of other sizes, does not differ by more than 5 per cent of itself from the fat percentage of the remaining milk as determined after thorough mixing."

Homogenization of milk is usually accompanied by fortification with vitamin D. Such fortification may be accomplished by feeding the cow high vitamin D containing materials such as irradiated yeast, exposing the milk in a thin layer to ultraviolet irradiation, or by the addition of vitamin D concentrates to the milk. The last mentioned process is most commonly practiced and yields a milk of 400 units of vitamin D per quart. Vitamin D milk is milk "which has been increased by an approved method to at least 400 U.S.P. units per quart."

Soft Curd Milk. A special milk sometimes offered by the dairy industry is soft curd milk. Soft curd milk may be obtained by selection of naturally soft curd products, homogenization, zeolyte treatment of the milk, boiling, addition of such colloids as gelatin or tannic acid, treatment with proteolytic enzymes, or the addition of citrate, pyrophosphate or metaphosphate.

The curd characteristics of milk may be determined by standardized procedures involving the addition of acid and pepsin or rennin to the milk and determining the weight necessary to move a curd knife into or out of the curd. Normal milks vary in their curd tensions between 15 and 150 g. Milk with curd tensions of 30 g. or lower are regarded as soft curd. Factors involved in determining the curd tension of milk are amount and dispersion of the fat, concentration of the casein and calcium, and the manner of their dispersion.

Flavored and Cultured Milk Drinks. Chocolate milk or chocolate milk drink is the only flavored milk drink prepared in substantial quantity by the dairy industry. Chocolate milk contains the legal requirements of fat for whole milk, whereas chocolate milk drink may be prepared from milk of 1 to 2 per cent butterfat content. In order to prevent the chocolate particles from settling out in the milk, stabilizers such as an irish moss extract, sodium alginate, starch, or a combination of these may be added to produce a nonsettling type of chocolate milk. Chocolate milk usually contains 1 to 1.5 per cent of cocoa and 5 to 7 per cent of sugar. Chocolate milks are soft curd.

Cultured milk or cultured buttermilk is another product of the fluid milk industry. Because cultured milks can be prepared in a uniform way by well controlled processes, it has largely replaced the buttermilk obtained from the churning of butter. Cultured buttermilk is made from pasteurized skim milk into which lactic acid-producing organisms have been inoculated and the acidity allowed to develop to about 0.8 per cent as lactic acid. Butter granules churned from sweet cream may be added to the cooled cultured milk in order to improve the appearance. Churned cultured buttermilk may also be prepared by use of milk containing about 2 per cent fat. Churning the product during manufacture results in producing butterfat granules in the final product. Salt to the extent of 5 ounces per 10 gallons of buttermilk may be added to impart flavor to the buttermilk. A flavorful cultured buttermilk may be produced by use of organisms that produce diacetyl and acetylmethylcarbinol in addition to lactic acid. Such organisms are *Leuconostoc citrovorus* and *L. paracitrovorus*.

There are also on the market a number of other fermented milk products that enjoy limited sale. Milk fermented with *Lactobacillus acidophilus* has been used for therapeutic purposes based on evidence that this organism is an inhabitant of the intestinal tract and will combat autointoxication caused by elaboration of toxic substances in the body by putrefactive organisms. Another fermented milk product is Bulgarian buttermilk (also known as *yoghurt* or *matzoon*). *Lactobacillus bulgaricus,* sometimes in combination with *S. thermophilus,* ferments the milk to yield a sharp-tasting product of 1.5 to 2.0 per cent lactic acidity. Other fermented milks are *kumiss* and *kefir* of Russian origin and *koeldermilk* used in Denmark and *leben* made in Egypt. These milks vary in their composition and in the organisms used. Lactic acid is a constituent of all of them and alcohol developed by yeasts is contained in some of them.

Separation of Milk. Milk has the property of creaming by gravity separation on standing. The formation of cream at the top of the milk bottle is a commonly observed physical process and is due to the difference in specific gravity between the fat and the aqueous phase. Cream appears to form more rapidly than can be accounted for on the basis of the diameters of the individual fat globules in milk if they were to follow Stoke's law. The explanation lies in the fact that the fat in milk exists in the form of clumps of globules and these clumps, rather than the individual fat globules, are involved. The creaming of milk accordingly proceeds in two phases: the clumping of the fat and the rising of the clumped fat to the top. Any processing that affects the conditions or forces on the fat/serum interface will affect creaming. Pasteurized milk should be cooled to 35 to 40° F. as clumping occurs most rapidly at this temperature. Storage of milk at 50° F. or higher decreases the cream volume because of the deformation of the soft fat at this temperature. Pumping or agitation of hot milk usually will not affect the creaming properties, but similar treatment of cold milk should be avoided because of the possibility of breaking up the clumped masses of fat. The cream volume on normal milk slowly decreases to a constant minimum after 24 hours. The fat content of the cream at this time will be 20 to 24 per cent and that of the layer below the cream line will average 0.3 to 0.4 per cent.

Cream. The legal standard for fat content of cream in the several states of the United States varies between 15 and 22 per cent, with the majority of states setting 18 per cent as the minimum. The United States Public Health Service defines cream as "a portion of milk which contains not less than 18 per cent milk fat"; light cream, coffee cream, or table cream are defined as "cream which contains less than 30 per cent milk fat," whipping cream as "cream which contains not less than 30 per cent milk fat," light whipping cream as "cream which contains less than 36 per cent milk fat," and heavy cream as "cream which contains not less than 36 per cent milk fat."

Commercially cream is prepared by passing milk previously heated to 90 to 95° F. through the cream separator. The invention of the cream separator by the Swedish engineer, Gustav De Laval, was one of the major developments of the dairy industry. The airtight separator is a hermetically sealed machine in which the whole milk, skim milk, and cream are under controlled pressure at all times. The whole milk is fed into the bottom of the separator bowl by means of a positive displacement supply pump which is synchronized with the capacity of the separator, the milk entering the bowl at a flow rate comparable to the speed of the rotating bowl. From the bottom of the bowl, the milk passes into a hollow distributor nut, from the ports of which it is forced upward through the perforations in the discs. These openings are located a short distance beyond the center of gravity, at which point separation begins, thus permitting the cream to find its way into the quiescent zone without disturbance from incoming whole milk. From here the cream passes from the revolving bowl into the stationary density control chamber, provided with external control whereby adjustment may be made readily to any desired fat content.

Other types of centrifugal separators are used, but they are all based on separating fat from the whole milk, the skim milk containing only about 0.10 per cent fat.

Cream from the separator is immediately cooled to about 50° F. and, when enough has accumulated, it is pasteurized with as little agitation as possible. Homogenization of cream is often used to eliminate or reduce the formation of a skim milk layer at the bottom of the cream bottle and to emulsify free fat or large fat globules that may have formed in the cream as a result of excessive agitation. Homogenization also imparts increased viscosity to cream and greater ability to color coffee. High pressures of homogenization may, however, cause feathering or curdling in the coffee.

The viscosity of cream is a general indication of the quality of cream from the consumers' standpoint. While the viscosity of cream increases with the fat content, creams of the same fat content may vary widely in viscosity due to the effects of other factors. Hening and Dahlberg[50] have developed a method of "rebodying" which markedly affects the viscosity of cream. Pasteurized cream, cooled to 40° F., then warmed to 80 to 84° F. in an internal tubular heater in 3 to 10 minutes, and again cooled to 40 to 48° F. in an internal tubular cooler in the same time showed a marked increase in viscosity. The result is attributed to the state of the fat globules as they approach a temperature of 80 to 84° F. from the liquid or solid form. This manner of influencing the viscosity is more marked with cream of high fat content than with cream of low fat content. Aging of cooled cream also operates to increase its viscosity.

Whipped Cream. The process of whipping consists of incorporating air into the cream to produce a fairly stable foam. The protein is probably denatured during the whipping process and contributes to the rigidity of the foam. Factors of importance in whipping cream are sufficient fat (36 to 40 per cent), aging of the cream (24 hours), cold temperature (fat must be solid at the whipping temperature), and a satisfactory whipping mechanism. Certain aids used by the housewife to prepare stable whipped cream are sodium citrate, sodium lactate, calcium acetate, and 0.2 to 0.4 per cent calcium sucrate (Viscogen), 0.35 per cent gelatin, and 0.2 to 0.25 per cent sodium alginate.

Getz, Smith and Tracy[37] have described another procedure for incorporating air into cream. This involves packing of the cream in containers under pressures of nitrous oxide gas. On dispensing the cream to atmospheric pressure, the gas leaves the cream solution to form small cells evenly distributed throughout the mass, which mass then becomes an aerated whipped product. Whipped cream of 200 to 600 per cent increase in volume (overrun) is obtained by this process. Since there is no evidence of fat clumping, the mechanisms of whipping in the aeration and in the mechanical whipping process are accordingly different. Combinations of nitrous oxide and carbon dioxide are also used in preparing whipping cream by the aeration process.

Cultured Creams. Cultured sour cream, also known as Jewish cream, usually has a fat content of 18 to 22 per cent. In manufacturing this product, cream is pasteurized at 180° F. for 30 minutes, homogenized at this temperature at pressures between 2000 and 3000 pounds, cooled to about 70° F. and 1 to 3 per cent of culture added. The inoculated cream may next be filled into open mouth jars or into cans in which containers the product is incubated at 68 to 72° F. until an acidity of about 0.6 per cent (as lactic acid) is reached. The sour cream is then cooled and aged 12 to 24 hours before marketing.

BUTTER

The fat of milk has long been regarded as its most intrinsically valuable constituent. The concentration in the form of butter has been practiced for many years as a means of storing this constituent of milk. The invention of the separator had a great influence on the development of the butter industry by providing a method for concentrating the fat in the form of cream which could easily be churned into butter. The United States production of butter in the year 1948 was 1,214,200,000 pounds, in the manufacture of which about 21 per cent of the milk supply of the country was used.

Butter sold in the United States must comply with certain requirements as established by act of Congress, March 4, 1923. This defines butter as "the food product usually known as butter and which is made exclusively from milk, or cream, or both, with and without additional coloring matter and containing not less than 80 per centum by weight of milk fat, all tolerances having been allowed for." Routine tests made in the manufacture of butter are fat, moisture, curd, and salt. A typical analysis of butter may be fat 80.3 per cent, moisture 16.1 per cent, curd 0.7 per cent and salt 2.9 per cent. Eastern markets prefer a light salt treatment (1.5 per cent), midwestern markets prefer a butter with about 2.5 per cent salt, and in the south a butter of about 3 per cent is desired. The Jewish trade demands a butter containing no added salt.

Wilster [126] and also Hunziker [57] describe the details of the methods for grading commercial cream for butter making. This cream may originate as gravity or centrifugally separated cream from the farm or as cream obtained from milk separated at the butter factory or creamery. The factors which determine the grade of cream are flavor, odor, appearance, acidity, age, and extraneous matter.

Cream Preparation. The first step in the preparation of cream for churning is the standaridzation of acidity. Special sweet grade cream may require no adjustment of acidity by the use of alkaline salts. Much cream however, requires acid reduction or neutralization. Neutralization as practiced commercially involves reducing the titratable acidity to 0.1 to 0.35 per cent as lactic acid. This reduction of acidity operates (1) to prevent fat losses resulting from churning pasteurized high acid cream, (2) to prevent the development of undesirable flavors in butter made from the high acid creams, and (3) to improve the keeping quality. The acidity at churning time is the factor that influences flavor and keeping quality, at which time the serum acidity of the cream should be not more than 0.35 per cent. Serum acidity is the acidity of the nonfat portion of the cream. The neutralizer is best added to the cream at 85° F. in the form of a slurry. The following materials are used as neutralizers: high, medium, or low magnesium limes, sodium carbonate or bicarbonate, or mixtures of the carbonates, and mixtures of soda ash and caustic soda. A common practice is to begin the neutralization with lime and to complete it with soda. The neutralized cream is then pasteurized by the holding method at 145 to 165° F. for 30 minutes, or by the short time high temperature method at 180° F. or above. A number of special pasteurization methods have been developed for butter which not only pasteurize, but remove from the cream such undesirable odors as feed or onion. Vacuum pasteurization involving injection of steam directly into the cream in a vacuum chamber has been described by several investigators and designated as "Impact Sterilization" by Grindrod,[43, 44] the "Super-deodorizer" by the Jensen Machinery Company, the "High Temperature Cream Pasteurizer" by Rogers,[93] "Vacuum Pasteurization" by Hammer, Horneman and Parker,[45] and the "Vacreator" by Murray.[72]

Pasteurization of cream for butter making not only destroys the microorganisms but also yields a cream of controlled churning characteristics and a butter of improved keeping quality. It also inactivates lipolytic enzymes which, if active in the butter, would cause the development of bitter and rancid flavors.

In efforts to remove feed and weed flavors from cream, various chemical treatments have been suggested. Among such treatments are use of chloramine T type compounds, treatment with hydrogen peroxide (Buddizing) treatment with Listerine, treating the cream, and churning the butter in atmosphere of carbon dioxide (Heathizing).[49] All these treatments are of doubtful value and none has found permanent application in the butter industry.

After pasteurization the cream is ready for ripening prior to churning. Cream ripening refers to the treatment which cream receives, if any, and the changes it undergoes in flavor, aroma, and texture between pasteurizing and churning. Commercial butter cultures added to the cream in ripening contain not only acid-producing organisms such as *S. lactis* but in addition, the associated organisms *L. citrovorus* and *L. paracitrovorus.* These organisms are capable of fermenting the citric acid of the cream to form the aroma-producing substances, diacetyl and acetylmethylcarbinol, the latter which on oxidation yields diacetyl. The flavor of butter is due not only to these compounds but probably also to a number of other materials such as acetic and propionic acids, acetaldehyde and others. Davies [24] found the diacetyl content of butter to affect its flavor as follows:

Amount of Diacetyl	*Flavor*
None	Flavorless
0.2 to 0.6 p.p.m.	Mild flavor
0.7 to 1.5 p.p.m.	Full flavor

Butter contains only a relatively small proportion of the diacetyl and acetylmethylcarbinol of the cream from which it was churned, the greater portions going to the buttermilk. In butter itself the aqueous phase contains larger amounts of these compounds than does the fat phase.

Cream may accordingly be ripened by action of starter as described, but starter development in the cream may result in the production of more acid than desired. In some cases, therefore, 5 to 7 per cent of starter may be added to the cream just before churning. The acidity is increased only slightly, and the flavor and aroma of the resulting butter will depend entirely on the degree to which flavor and aroma-bearing compounds were present in the starter. Instead of adding starter to the cream before churning, it may also be added to the butter after churning.

Ruche [98] has described a method of preparing a starter distillate rich in diacetyl. Use of this material in such amounts as to limit the diacetyl content of the butter to 4 p.p.m. appears to be satisfactory. However, the mere working of these materials into the butter fails to fuse them with the butter constituents as completely as when they are formed in the cream and churned into the butter.

Churning. The process of churning involves agitation of the cream until it yields granules of butter which coalesce to form masses of butter. There are two outstanding theories of churning—the foam theory and the phase inversion theory. In accordance with the foam theory, the churning process causes the incorporation of air into the cream with the resultant formation of a foam. Rahn[85] has suggested that there is close packing of the fat globules in the froth of *lamellae* in the fat-rich foam of churned cream, finally resulting in fat clumps. The protein in the lamellae gradually assumes a solid character until further churning destroys the structure and the foam collapses. There occurs a precipitation of the foam-colloid bringing about destabilization of the fat emulsion and the coalescence of the destabilized fat globules. This theory fits many of the observed phenomena of churning. Churning at low temperature does not yield butter because the solid fat globules do not cohere. A full churn with no air space will not yield butter even after several hours of churning.

In accordance with the phase inversion theory, Fischer and Hooker[31] consider the cream an emulsion of fat in hydrated protein and the tendency to form butter is enhanced by the dehydration of the protein. "Since the hydrated colloids tend to collect in the surface layers between the fat particles and the aqueous phase of the cream, efforts are made to break these layers, and so to hasten coalescence of the fat globules and churning. The combined efforts therefore bring about a progressive increase in the concentration of the oil with a decrease in the concentration of the hydrated colloid until the instability of the oil-hydrated colloid emulsion becomes so great as to "break" and yield the hydrated colloid in fat emulsion which is called butter." Palmer[78, 79] supports this theory from observations on the inversion of emulsion type by staining the fat globules with oil-soluble dyes before churning and by observing the sharp change in electrical conductivity at the "breaking" point.

These theories of butter making in combination with experimental facts led Holm[56] to conclude that butter consists of fat globules, air bubbles and water droplets, each surrounded by protector films and dispersed in a mass of free fat. Among the factors which affect the churning properties of the cream are size and dispersion of the fat globules as influenced by heat treatment, cooling of the cream preparatory to churning, agitation in the churn, chemical composition of the butterfat, stage of lactation, breed of cow, fat content of the cream, viscosity of the cream, and fullness, design, and speed of operation of the churn. Cream of 30 to 36 per cent fat content cooled to 40 to 56° F. before churning (fat globules at least partially solidified) with the churn about half full of cream, should produce butter after a churning period of 30 to 45 minutes. At the end of churning the butter is freed as completely as possible from buttermilk and the butter washed to further remove buttermilk. The butter is then salted to the desired degree and butter color added to standardize this characteristic, such standardization being required because of the variability in carotene content of the butter from season to season. Butter colors used are annatto, colored substances extracted by oil from the annatto plant (*Bixa orellana*) or such oil-soluble dyes as Yellow A B or Yellow O B. The butter is also standardized as to moisture content at this point.

The butter-making operation that has been described is the one commonly used in the United States. At the present time experimental work is being done, and some butter is being made commercially by a number of other butter making procedures. These are described by Hunziker[57] and by Wilster,[126] who also give excellent discussions of the butter industry. Most of these methods involve reseparation of the cream to yield a product of high fat content (90 per cent) which product is standardized to the proper color, moisture, and salt content.

Another butter-making procedure that obviates the conventional process is based on using plastic cream. Plastic cream is obtained by passing regular cream through a high-speed centrifuge to yield a cream of 80 per cent fat content. Plastic cream is itself a product of commerce being used primarily in the ice cream industry. In the converting of plastic cream to butter, it is only necessary to change the structure or invert the phases, add salt, and standardize since plastic cream already contains sufficient fat.

Butter is the chief form in which milk fat is concentrated. The patents of North[75] and of Riggs[91] deal with the production of a product about 99.5 per cent milk fat. The Riggs process involves adjusting the cream to pH 3.8 to 4.8, and simultaneously raising the temperature to at least 200° F., centrifuging to produce an intermediate product of 80 to 85 per cent fat content, maintaining the temperature of this product at 200° F. and diluting with hot water, preventing re-emulsification of the fat by use of an emulsion inhibitor and centrifuging the intermediate to produce a milk fat of 99.5 per cent fat. Milk fat of this type is used in the food industries and finds special use for re-emulsification with dry milk solids and water to produce a reconstituted milk in places where fresh milk is not available.

CHEESE

Cheese production in the United States in 1948, exclusive of cottage and cream cheese, was 1,177,669,000 pounds. It is estimated that about 500,000,000 pounds of cottage plus cream cheese were produced. The cheese industry is based on concentrating another portion of the milk, the casein plus the fat or in some cases only the casein.

The mechanism of the conversion of casein first into curd and finally into cured cheese is not completely understood. Rennin, a coagulating enzyme contained in rennet extract obtained from the fourth stomach of the young calf or from the digestive stomachs of sheep or pigs, is used in obtaining the actual curd in cheese making. The casein, existing in milk as calcium caseinate, is believed to be coagulated in the cheese-making process in three steps. The first step effected by the rennin is the change of calcium caseinate into uncoagulated calcium paracaseinate. The second step is the production of acid by lactic acid bacteria in the milk, which acidity operates to liberate calcium ions. The third step involves the physical and chemical action of the soluble calcium ions to yield the paracaseinate coagulum (curd). Many factors affect rennin coagulation, such as the presence of calcium ions, reaction of the milk, milk solids concentration, presence of acid, alkaline or neutral salts, time, and enzyme concentration. Coagulation is hastened by free acidity, acid salts, high temperatures, and the presence of finely divided inert solids, such as starch. The opposite effect is produced by neutral or alkaline salts, and by previous holding of the milk at elevated temperatures.

The casein performs three functions in cheese making: in its coagulation it imprisons fat globules and phosphate salts in the curd and holds them firmly during cheese making; it retains water and whey within the curd in amounts to permit proper development and ripening in the cheese; and it is the material which gives rise to characteristic flavors when the cheese ripens.

Cheese Varieties. Doane, Lawson and Matheson[26] describe more than 400 varieties of cheese. These varieties owe their differences to a limited extent to differences in the milk but primarily to variations in the essential conditions during the process of cheese making. The great variety of conditions to which curd from milk can be subjected make possible the production of cheese of almost infinite variety. These conditions include moisture content of the curd, relative fat and protein content, temperature combinations to which the ripening curd can be subjected and the microorganisms which can be inoculated into the curd and those which persist due to the conditions of moisture and temperature to which the curd can be subjected. Data on a great many cheese varieties are given by Doane, Lawson and Matheson, whereas Van Slyke and Price[116] and Sammis[99] describe the manufacture of the important commercial varieties of cheese.

In general, cheese varieties may be divided into three groups, hard, semi-hard, and soft types. The most common hard types are Cheddar and Swiss; semi-hard varieties are Brick, Muenster, and Limburger; and soft types are Cottage, Cream, Brie, and Camembert. Although many hundreds of cheese varieties exist, it is considered that the varieties fall into about

18 classes. The United States government is in the process of setting standards of identity for the industry.[30] The proposed standards cover the following cheeses: Cheddar, washed-curd, soak-curd, Colby, stirred-curd granular, Swiss, brick, Muenster, Edam, Gouda, blue mold, Camembert, Limburger, Monterey, high moisture jack, Provolone pasta filata, Parmesan, Monte, Modena, Romano, Asiago fresh, Gorgonzola, Cook, hard, semi-soft, soft ripened, Noekkelost or kuminost, pasteurized process, pasteurized process with fruits, vegetables, and meats, cold pack, club, comminuted, cold pack cheese foods, and the same with fruits, vegetables, and meats. Standards for manufacturing grade of the first seven types of cheese listed are also given. These standards of identity give the fat and moisture content of the cheese, as well as methods of handling the milk, of coloring the cheese, adding starter and rennin to the milk, and determining fat and moisture in the cheese.

As examples of cheese making, the production of cottage cheese, a soft unripened variety, and Cheddar or American cheese, an important ripened cheese of the hard type will be described here.

Soft Cheeses. Cottage cheese is one of the principal unripened soft cheeses made in the United States. The United States Public Health Service defines cottage cheese as ''the soft uncured cheese prepared from the curd obtained by adding harmless lactic acid-producing bacteria, with or without rennet, to pasteurized skim milk, concentrated skim milk, or nonfat dry milk solids. It contains not more than 80 per cent moisture.'' Creamed cottage cheese is defined similarly but it must contain not less than 4 per cent of milk fat by weight. This cheese is usually made from pasteurized skim milk. This milk is brought to a temperature of 68 to 72° F. and then 0.2 to 5 per cent of starter is added. Calcium chloride to the extent of 1 to 4 ounces per 1000 pounds of milk is sometimes used to aid in obtaining a firm curd. Rennet extract at the rate of 0.75 to 1.25 cc. or pepsin at the rate of 0.5 g. per 1000 pounds of milk may also be used in combination with the starter in cottage cheese making. After 7 to 16 hours, depending on the quantity and activity of the starter, the milk coagulates to form a firm curd. This curd is cut into small cubes with curd knives. One type of knife cuts the curd into horizontal layers and another cuts vertically across these layers from top to bottom. The cheese milk at the time of cutting will have an acidity equal to pH 4.6 or the whey will have an acidity of about 0.6 per cent as lactic acid. After cutting, the curd is firmed by slowly raising the temperature to about 115 to 120° F. Heating to this temperature requires 60 to 90 minutes and a holding period of 30 minutes is usually required to firm the curd properly. The curd is then washed with successive washings of cold water. Too complete washing may produce a flavorless curd, hence control of the washing procedure is necessary. The washed curd is next salted by spreading salt over the curd surface and working it into the curd mass. The amount of salt varies between 0.75 to 1.50 per cent depending on market requirements. The final cheese contains 20 to 30 per cent of solids, mostly protein. A yield of 12 to 18 pounds (average 15) of cottage cheese is obtained from 100 pounds of skim milk.

For creamed cottage cheese, sufficient pasteurized cream is added to give the product a fat content of 4 to 6 per cent. Baker's cheese is manufactured in a similar manner to cottage cheese except the coagulum is not cut or heated but transferred to draining bags and pressure applied to the bags to remove the whey. These are examples of how the cheese making operation may be varied to modify the character of the final cheese.

Hard Cheeses. In the making of Cheddar cheese, the pasteurized milk is contained in rectangular jacketed vats where the temperature of the milk is brought to 86° F. Starter is next added to the extent of 0.25–5 per cent and thoroughly incorporated into the milk. The starter is an actively growing culture of lactic acid-producing organisms. The acid-producing organism usually predominating in starters is *Streptococcus lactis* and associated with these organisms are such organisms as *Leuconostoc citrovorus* and *L. paracitrovorus* which produce flavor contributing compounds mentioned previously from the citrate present in the milk. The starter in the cheese milk operates to produce acidity in the milk. When the acidity has reached a value of 0.17–0.22 per cent as lactic acid, the rennet is added at the rate of 3 ounces of rennet per 10,000 pounds of milk (the rennet being diluted with 40 times its quantity of water). The milk is left undisturbed and the curd begins to form in 15 to 20 minutes and in 30 to 40 minutes, the curd is ready to cut into cubes as described for cottage cheese.

The cubes of curd are kept afloat in the whey by stirring gently with paddles to prevent coalescing in the bottom of the cheese vat. This initiates firming of the curd but the temperature must be raised to complete this process. As the temperature is increased, the acidity increases and this also accelerates curd firming. The temperature is usually raised at the rate of 2° F. every 5 minutes. For whey of 0.12, 0.13, 0.14, and 0.15 per cent acidity, the heating periods at the rate given are usually 60, 40, 30, and 20 minutes, respectively. At the end of the heating or firming period the curd pieces should have contracted to half their original size, the curds should be firm and springy, they should feel hard to the touch, should show fine threads when touched to a hot iron and pulled away (the hot iron test), and the whey surrounding the curd should have an acidity of 0.16 to 0.175 per cent as lactic acid. At this point in the process the whey is removed by piling the curd to the side of the vat and drawing off the whey through a gate valve at the end of the vat.

The distinctive operation in making cheddar cheese is the cheddaring process. This operation consists in piling, matting, or packing the curd and cutting it into strips and continuing the operation of piling, cutting, and repiling. The purpose of the cheddaring is to permit removal of moisture and to allow the formation of a characteristic body and texture. The texture changes so that the curd acquires a fibrous condition known as chicken-breast texture. Cheddaring is considered complete when the whey flowing from cheddared curd has an acidity of 0.6 per cent as lactic acid and when the hot iron test gives threads 0.5 to 1 inch in length.

The satisfactorily cheddared curd is next milled into small pieces so that excess whey can be further removed and the curd can be cooled, salted and distributed into hoops for pressing. Salt is added to the curd to the extent of 1.75 to 3.25 pounds per 1000 pounds of original milk used. Unripened cheese usually contains 0.6 to 1.0 per cent of salt which percentage increases as the cheese ripens due to moisture loss. Salt improves the flavor of the cheese, aids in removing whey, hardens and shrinks the curd, and checks or retards the further formation of acid and undesirable types of fermentation.

The milled cheese ready for pressing is placed in hoops of various shapes, known as longhorns, prints, daisies, flats, twins, cheddars, young Americas, picnics, etc. They are usually cylindrical, from 5 to 15 inches in diameter and weigh from 1 to 70 pounds. A horizontal press is used and 10 or 15 hoops of cheese are pressed in one operation. The cheese is held in the presses for 24 hours during which time the pressure is uniformly and continuously applied.

After pressing, the cheese goes to the ripening or curing room where it is held for periods varying from 2 or 3 months to 2 years. During ripening there is an increase in water-soluble nitrogen, amino nitrogen, ammonia nitrogen and fatty acids. Peterson, Johnson and Price [81] show that milk lipase is absent in freshly made cheese but that 5 to 20 days after making, lipases of bacterial origin begin to appear in the cheese. These lipases are accordingly considered responsible for the hydrolysis of fat that occurs during cheese ripening. The same workers find that active proteinase in ripening cheese is of bacterial origin. In studying the factors involved in flavor development in cheddar cheese Dahlberg and Kosikowsky [19, 20] were able to find no relationships among intensity of flavor, total volatile acidity, water-soluble protein, pH, and age of the cheese. They did find a positive correlation between water-soluble nitrogen and age of the cheese. Further studies indicated a semilogarithmic relationship between tyramine content of the cheese and age. Tyramine (β-p-hydroxyphenyl ethylamine) is not a Cheddar cheese flavor compound but serves as a means of measuring a factor that accentuates flavor development. A combination of lactic and *Streptococcus faecalis* starters in cheese produces the largest amount of tyramine. Defects which must be guarded against in the manufacture of Cheddar cheese are discussed by Van Slyke and Price.[116]

By modifying the cheese process that has been described, a great variety of cheeses can be produced.

Blended Cheese Products. "Pasteurized," "Processed," or "Pasteurized Blended" cheese may be made from the various types of cheese. Carefully graded cheese of the type desired is ground to permit the cheese to melt readily and then placed in specially designed steam jacketed kettles. Some cheese will not produce the desired qualities unless an emulsifying agent is used. Commonly used emulsifiers are various sodium phosphates, sodium citrate, sodium tartrate, sodium potassium tartrate, and mixtures of these salts. Lactic, citric, acetic, hydroxyacetic and phosphoric acids may be used to control the pH of the final product. Water approximately equivalent to that lost by evaporation is added to the pasteurizing kettle. The water contains, dissolved in it, the emulsifying salts at the rate of 0.5 to 3 per cent of the cheese. The ground cheese mass is then heated between 140–160° F. with agitation to form a smooth glossy creamy mixture. When the heated mass has the desired properties it is conveyed to filling machines or weighed directly into packages. Cheddar, Swiss, and Limburger are often used in making pasteurized blended process cheese.

Certain cheese foods are also manufactured by the cheese industry. Such cheese foods are usually blends of cheese with whey solids and nonfat milk solids. The combination is such as to give the final product the same calcium and phosphorus content as fluid milk. Cheese foods may also contain one or more of the following sweetening agents: dextrose, sucrose, maltose, corn syrup solids, lactose, and hydrolyzed lactose. The same procedures and emulsifiers are used for the cheese foods as for the pasteurized processed cheeses. According to proposed definitions, a cheese food may contain not more than 44 per cent of moisture and not less than 23 per cent of milk fat. Cheese foods have excellent nutritional value.

Whey. Whey is the liquid remaining after removing the curd from the cheese milk. The fat contained in the whey is removed by centrifugal separation. Whey then has the following composition: total solids 6.85 per cent, protein 0.89 per cent, fat 0.24 per cent, lactose 4.81 per cent, ash 0.51 per cent, and acidity as lactic 0.19 per cent. Most of the whey goes to the production of by-products, such as animal feeds, etc.—see pages 145, 152. A very small amount is used to manufacture a concentrated whey product known as "primost" or "mysost," a Scandinavian cheese product.

CONCENTRATED MILK

Nicholas Appert in 1796 found that it was possible to condense milk to two-thirds of its original volume by evaporating a portion of the water with heat. The strained product was bottled and sterilized by immersing the bottles in boiling water. Gail Borden first prepared concentrated milk on a commercial basis in this country in 1858.

Condensed milk may be divided into two classes, sweetened condensed, and unsweetened condensed. Both may be made from whole milk or from skim milk, and both may be packaged in cans for the retail consumers and other food manufacturers. The term *condensed* milk usually designates the sweetened type, the unsweetened product being referred to as *plain condensed*. *Evaporated milk* is the whole nonsweetened product sterilized in cans. The compositions of the various concentrated products of milk are given in Table 47.

TABLE 47. COMPOSITION OF CONDENSED AND EVAPORATED MILKS

Milk Products	Total Solids %	Water %	Milk Solids %	Fat %	Protein %	Lactose %	Ash %	Sucrose %
Sweetened Condensed								
U.S. Standard [8.5% fat, 28% MS]	72.0	28.0	28.0	8.5	7.5	10.5	1.5	44.0
Overstandard	75.5	24.5	33.5	9.5	8.9	13.1	2.0	42.0
Evaporated								
U.S. Standard [7.9% fat, 18% non-fat milk solids]	25.9	74.1	25.9	7.9	6.7	10.0	1.4	0.0
High Solids	32.5	67.5	32.5	9.5	8.7	12.4	1.9	0.0
Plain Condensed Milk	30.0	70.0	30.0	8.5	7.8	11.9	1.8	0.0
Skim Condensed								
Sweetened U.S. Standard [24% MS]	71.5	28.5	24.0	0.5	8.8	12.7	2.0	47.5
Plain U.S. Standard	20.0	80.0	20.0	0.3	7.3	10.8	1.6	0.0
Plain Skim Condensed [usual commercial product]	30.0	70.0	30.0	0.5	11.0	16.2	2.4	0.0
Condensed Buttermilk	28.9	71.1	28.9	1.95	10.61	13.01	3.33	0.0
Concentrated Sour Skim milk	28.0	72.0	28.0	1.17	10.19	15.51	2.13	0.0

Federal standards have been set for several of these concentrated milks as indicated in Table 47. Over-standard sweetened whole condensed milk contains 9.5 per cent fat, 33.5 per cent total milk solids, and 42 per cent sucrose. Investigations of Webb, Bell, Deysher and Holm[118] indicated that an evaporated milk of 32 per cent total solids could be prepared which is higher than the standard product of 25.9 per cent total solids.

The vacuum pan is the unit around which the concentrated milk industry is built. Hunziker[58] describes the many types of vacuum pans and the vacuum arrangements that are used in the industry. Most vacuum pans are equipped with entrainment separators which reduce milk solids loss to a minimum and are equipped with sampling devices so that the product being manufactured can be tested and controlled during operation. Most equipment for processing the milk is constructed of 18-8 stainless steel, other chrome-nickel alloys containing 13 per cent chromium, 80 per cent nickel, and 6 per cent iron also being used.

Sweetened Condensed Milk. Sweetened whole condensed milk is condensed to a volume ratio of 2.33 to 2.75 to 1. Sucrose or sucrose plus dextrose is used as the sweetening agent with the final sugar content averaging 40 to 45 per cent. The Federal definition provides that sweetened condensed milk shall contain not less than 8.5 per cent of fat and not less than 28 per cent total milk solids. Milk standardized to the proper ratio of fat to nonfat solids is preheated in hot wells and the sugar is added at this point. Preheating the milk facilitates controlling the milk in the vacuum pan, pasteurizes the milk, inactivates milk enzymes, and provides a means of preventing age-thickening. The age-thickening that occurs in sweetened condensed milk is apparent in the changing of the product from a smooth fluid to one that is viscous or jelly-like in nature. According to the work of Stebnitz and Sommer,[106] changes in the milk proteins are involved in this phenomenon. It appears that milk heated within the temperature ranges 140 to 167° F. yields a sweetened condensed product of low viscosity which does not undergo age-thickening. At preheating temperatures below 150° F. there may even be age-thinning with the possibility of lactose crystals settling to the bottom of the container because of the low viscosity. Preheating at 175 to 212° F. increases the age-thickening tendency, whereas heating at a temperature substantially higher than the boiling point decreases it.

Sugar is added to milk in the hot wells to yield a product that on concentration will keep without requiring heat sterilization. Preservation by addition of sugar is possible because of the high osmotic pressure of the final product. Sucrose was originally used in the manufacture of sweetened condensed milk but Ramsey, Tracy and Ruehe[88] have shown how dextrose can be used to replace a part of the sucrose. Difficulties that have been encountered in the use of dextrose were the development of a brown color and an accelerated age-thickening. The reaction responsible for the brown color is thought to be one between the aldehyde of the sugar molecule and the tryptophan of the milk protein. By adding the dextrose dissolved in water to the batch of sweetened condensed at the end of the concentrating operation, about 25 per cent of the sucrose can be replaced with dextrose.

In order to have satisfactory keeping quality, the concentration of the sugar dissolved in the water of the final product should be 62.5 to 64.5 per cent. A sweetened condensed product containing 28 per cent of milk solids and 45 per cent of sugar and a water content of 27 per cent will accordingly show a sugar content of 62.5 per cent in the water. Manufacturers of bulk products have adopted a tentative standard of 30 per cent milk solids and 42 per cent sugar for their products.

The calculated quantity of sugar is added to the milk in the hot well and the mixture concentrated in the vacuum pan, samples being withdrawn from the pan for specific gravity tests either by use of a special pycnometer or by a Baumé hydrometer. The specific gravities for any desired composition can be calculated from the following formula:

$$\text{Specific gravity of sweetened condensed milk at } 60^\circ\text{ F.} = \frac{100}{\frac{\%\text{ fat}}{\text{sp. gr.}} + \frac{\%\text{ solids-not-fat}}{\text{sp. gr.}} + \frac{\%\text{ sugar}}{\text{sp. gr.}}}.$$

Sharp and Hart [101] give the specific gravity of milk fat as 0.930 and that of solids not fat as 1.608. The specific gravity of sucrose is 1.589.

At the end of the condensing operation the batch is removed from the vacuum pan. The manner in which the product is handled at this point is of much importance in determining its properties. Sweetened condensed milk is a supersaturated solution of lactose, but at the temperature of condensing (120 to 135° F.) there is relatively little lactose present in excess of saturation. As the temperature is reduced supersaturation increases, and the rate of crystallization is offset by the increased viscosity of the sweetened condensed product.

The procedure for effecting proper crystallization of lactose involves reducing the temperature of the batch from the pan to 85° F. rapidly, seeding with small lactose crystals and holding for about one hour at 85° F. with slow agitation during this period.

By this procedure most of the lactose that exists in milk over the point of saturation is forced to crystallize in large numbers of small crystals. This results in a product of smooth body, and large lactose crystals are not likely to form and to settle. This procedure for lactose crystallization takes advantage of the properties of the various crystalline forms of lactose and the conditions for their crystallization. Lactose is present in solution in two forms, α- and β-, only the α-form of which crystallizes out in the manufacture of sweetened condensed milk. In solutions at equilibrium, α- and β-lactose are present in definite ratio. At the point where the α-form begins to crystallize out, more β- must change to the α-form in order to maintain the equilibrium. At the point of maximum crystallization of lactose, 85 to 90° F., this succession of crystallization and mutation proceeds until the equilibrium at that temperature exists for the crystallized α-lactose hydrate and the dissolved α- and β-lactose.

The cooling of sweetened condensed milk by the batch system has been described. The continuous flow system, the combined batch and continuous system and the vacuum systems may be used in controlling the crystallization of lactose and all these systems are operated in accordance with the principles discussed for the batch system. On completion of the crystallization, the product is further cooled to 65–70° F. and packed in cans for case goods or in barrels for the bulk product. The production of canned sweetened condensed milk is 1947 was 158,453,000 pounds and for the bulk product 62,160,000.

Sweetened condensed skim milk is produced for use by bakers, confectioners, and other food industries. In 1947 production totaled 553,295,000 pounds. The same conditions apply to the manufacture of this product as for sweetened whole condensed milk. The product is usually packed in barrels which are stored at 40 to 60° F. until shipped. The usual composition of sweetened skim condensed is 30 per cent nonfat milk solids, 42 per cent sugar and 28 per cent water. Age-thickening is a more difficult problem with the skim product due to higher nonfat milk solids concentration. The preheating factors that govern age-thickening must accordingly be given special consideration. In order to produce a satisfactory product for the baking industry, the milk must be given adequate heat treatment. Careful adjustment of heat treatment is therefore necessary in order to impart satisfactory baking quality without accelerating age-thickening. Low temperature storage, at 35–40° F. of the product retards the age-thickening.

Evaporated Milk. Evaporated milk, as provided by Federal definition, may contain not less than 7.9 per cent fat and not less than 25.9 per cent total solids. The product reaches the market in hermetically sealed cans of 3 sizes; 6 ounces, 14½ ounces, and 1 gallon. Production in 1948 was 3,435,000,000 pounds equivalent to about 6.2 per cent of the milk supply.

In the manufacture of evaporated milk the usual practice is to heat the standardized milk to 200° F. or to boiling for 10 to 25 minutes before drawing into the vacuum pan. The preheated milk is then condensed to the desired solids content in a vacuum pan in the same way as for sweetened condensed milk. The sampling and testing of evaporated milk during concentration is more readily accomplished than for the sweetened product because the viscosity is so much lower that it facilitates the determination of the specific gravity with the Baumé hydrometer. The following formula can be used to calculate the specific gravity for a given solids content:

$$\text{Specific gravity} = \frac{100}{\frac{\%\ \text{fat}}{0.93} + \frac{\%\ \text{solids-not-fat}}{1.608} + \frac{\%\ \text{water}}{1}}$$

Some evaporated milk plants operate with the batch condensing process, others with the continuous process. In the latter case the removal of milk from the evaporator is synchronized with the inflow of milk. It is usually the practice to over-condense slightly so that standardization to the proper solids content can be made by the addition of water.

Evaporated milk is commonly fortified by the addition of vitamin D. There is advantage in providing vitamin D in the same food that is rich in calcium and phosphorus. The Food and Drug Administration [29] has accordingly established legal standards which provide that evaporated milk may contain vitamin D as an optional ingredient in such quantity as will increase the vitamin D content to not less than 7.5 U.S.P. units per ounce. This unitage is equivalent to 240 units per quart of evaporated milk. The council on Food and Nutrition of the American Medical Association has granted its seal of acceptance on evaporated milk containing 800 U.S.P. units of vitamin D per quart.

Milk contains some natural vitamin D and also provitamin D as cholesterol, capable of being activated by ultraviolet irradiation to have antirachitic properties. The evaporated milk may accordingly be irradiated by light from the carbon arc or the hot or cold mercury quartz vapor arc, one such procedure being that of Trebler.[113] Due to the low rate of flow required to allow production of 800 U.S.P. units of vitamin D per quart of the evaporated milk, manufacturers have largely practiced fortification with vitamin D concentrate rather than irradiation. Concentrates of two types are available, one in corn oil or other oil requiring homogenization before it can be distributed properly in the milk, the other in which the vitamin in butter oil or other oil is already emulsified with milk solids. Both vitamin D_2 (irradiated ergosterol) and vitamin D_3 (irradiated 7-dehydrocholesterol) are available in these forms.

After concentrating the milk and adding vitamin D, if desired, the milk is homogenized to reduce fat globule size so that fat separation will not occur in the final canned product. The homogenized milk is then filled into cans and sterilized. The sterilizing process must provide a temperature-time exposure that is lethal to even the most resistant organisms in the milk. In commercial practice, it is recommended that sterilization be conducted by heating to 240° F. and holding for 20 minutes, the time to attain 240° F. being not more than 20 minutes nor less than 15 minutes. The heating is conducted by steam under pressure, either in batch or continuously operating equipment. Immediately after sterilizing the cans are rapidly cooled. It is sometimes necessary to shake evaporated milk for a short time in order to remove a slight livery condition that may have developed as a result of sterilization.

Heat stability or relative resistance of the milk to coagulation in the sterilizer is a difficulty encountered in manufacturing evaporated milk. Webb, Bell, Deysher and Holm [118] have measured heat stability by determining the time necessary to initiate coagulation at 239° F. Factors operating to affect heat stability are of two types: those inherent in the milk such as chemical properties and freshness of the milk, and those imparted to the milk by the manufacturing process. Increase in acidity or protein concentration increases the susceptibility of the milk to coagulation. The acidity of evaporated milk is increased 0.05 to 0.1 per cent by sterilization. Both casein and lactalbumin are involved in heat coagulation and their concentration in evaporated milk increases the susceptibility of the milk to coagulation. Some milks may also contain rennin-like enzymes (chiefly of bacterial origin) which operate to cause coagulation of the milk proteins.

Salt balance of milk is another factor affecting the stability of the milk to heat. Instability to heat is usually due to an excess of calcium or magnesium in the milk; hence the heat stabilizers used commercially are almost always phosphates or citrates because these anions precipitate calcium and magnesium. When difficulty with heat stability occurs in commercial operations, it is the practice to determine the amount of stabilizer required by preliminary trials in a pilot sterilizer.

Several manufacturing steps modify heat stability. These include variations in forewarming temperature and time, concentration of milk solids and homogenization. The effects of forewarming have been discussed in connection with sweetened condensed milk. Homogenization tends to decrease only slightly the heat stability of the milk. The higher the milk solids with attendant higher concentration of milk protein, the more sensitive will the milk be to heat coagulation.

A certain body or viscosity is desirable in an evaporated milk to give the product fullness of character and to prevent fat separation on storage of the milk. The factors that affect protein coagulation in the milk are the same ones that affect the viscosity. Evaporated milk usually becomes thinner in body on storage but on storage at temperatures below 60° F. the effect is slight.

The brown color that appears in evaporated milk or that increases on storage is due to a protein-lactose reaction. This reaction is accentuated when the milk is processed at higher temperatures or when the milk is stored at abnormally high temperatures.

Evaporated milks have a flavor characterized as "cooked." Gould[39] found that the cooked flavor is due to the formation of sulfur compounds from milk protein and that a close relationship exists between cooked flavor and hydrogen sulfide liberation in the milk or between the flavor and the formation of sulfhydryl compounds.

Sometimes a white granular precipitate forms in cans of evaporated milk. This deposit, largely calcium citrate or tricalcium citrate, is associated with high solids evaporated milk, storage of the product, variation of the milk itself with season of production and advancing lactation period.

Bulk plain condensed skim milk is unsweetened milk concentrated in ratios 2.5 to 4.0 to 1. The product most generally manufactured has a total solids content of about 30 per cent. This product is manufactured in the same way as evaporated milk but may be subjected to considerable variation in the preheating process. Johnson and Ward[62] have shown that excellent baking properties may be imparted to such a product by preheating the milk to 185° F. and holding for 15 minutes even though the viscosity of such milk is low and comparable to milk preheated to 145° F. which is quite unsatisfactory for baking.

A modification often made in the application of heat to milk is exhibited in the product known as superheated condensed skim milk. This product is prepared by preheating milk no higher than 160° F., condensing to 30 per cent solids and then passing steam into the milk so that it is rapidly heated to 185–195° F. A great increase in viscosity results from this treatment. Care must be used in preparing this product, as coagulation of the protein is likely to occur if it is held too long at the high temperatures. As soon as the desired body is obtained, the batch is rapidly cooled to 135° F. or less by increasing the vacuum. On completion of the cooling, the product is placed in cans. The superheating process can also be applied to whole condensed milk. Ice cream manufacturers and bakers find greatest use for superheated condensed products.

The production of bulk whole condensed milk in 1947 was 133,675,000 pounds, and for the skim condensed product was 400,170,000 pounds.

Condensed Whey and Buttermilk. Whey remaining from the manufacture of cheese may be concentrated to yield several types of product. Ramsdell and Webb[86] have developed the following procedure for the manufacture of sweetened condensed whey. Fresh sweet cheese whey (Cheddar or Swiss) or rennet whey is pasteurized, then concentrated in the vacuum pan in the usual way, sucrose being added on an equal basis to the whey solids. The product is condensed to a solids content of 76 per cent and then cooling and crystallization are conducted in such a way as to produce small lactose crystals as has been described for sweetened condensed milk. Sweetened condensed whey is used in the food industries. Ramsdell and Webb[86] have suggested its use in special candies and fruit whips because of its marked whipping properties.

Plain condensed whey is manufactured primarily as an animal feed, the total solids content of the product varying between 35 and 70 per cent. The American Feed Control Officials direct that standard condensed whey shall contain not less than 62 per cent total solids. Webb and Hufnagel[120] have given methods for preparing condensed whey and density tables related to total solids for use in the manufacture of condensed whey. Because of the high proportion of lactose in whey there is danger of crystallization of the lactose during condensing. A satisfactory procedure involves drawing the concentrated product from the evaporator as a clear syrup, cooling to about 90° F., and seeding with lactose crystals to yield a smooth-bodied final product.

Concentrated cultured whey has the same standards for total solids as plain condensed whey. In making this product the fresh whey is pasteurized at 195° F., cooled to 105° F., and cultured with about 5 per cent of a lactic acid-producing culture such as *Lactobacillus bulgaricus* or *L. acidophilus* and held until the acidity is about 1 per cent. This product is then condensed to the desired solids content and handled as for the non-cultured product. The acidity of cultured concentrated whey is 10–12 per cent as lactic acid and this acidity gives the product excellent keeping quality.

Semisolid buttermilk or condensed buttermilk is manufactured from buttermilk available from creameries where butter is made. Fluid buttermilk is assembled in large tanks and the acidity allowed to develop, the acid buttermilk then being heated to about 185° F. and concentrated in a vacuum pan to 27–30 per cent solids. A typical analysis of condensed buttermilk is 28.9 per cent total solids, 1.95 per cent fat, 10.61 per cent protein, 3.33 per cent ash, 13.01 per cent lactose, and 5–6 per cent acid as lactic. The acidity of this product also operates to give it keeping quality. In 1945 the production of concentrated buttermilk was 160,401,000 lbs.

Rogers[94] has also described the manufacture of a concentrated sour or cultured skim milk. Essentially the process consists in adding an acid-producing starter to skim milk and then proceeding as for condensed buttermilk. An average analysis of cultured skim milk is 28.0 per cent total milk solids, 1.17 per cent fat, 10.19 per cent protein, 2.13 per cent ash, 15.51 per cent lactose, and 5–6 per cent acid as lactic acid. In 1945, 12,250,000 pounds of this product were manufactured.

Plain condensed whey, concentrated cultured whey, condensed buttermilk, and cultured skim milk are produced for the feed industry and are excellent feeds for hogs and poultry.

Miscellaneous Fluid Milk Products. The preservation of fluid milk by freezing has recently been subjected to much investigation by Babcock[6] and his associates. They report that frozen homogenized milk, containing 2 g. of sodium citrate and 0.1 g. of ascorbic acid per liter and stored at − 17.8° C., was satisfactory in body and flavor for 105–145 days. Frozen condensed milks have also been investigated. Doan and Leeder[25] suggest the following procedure for processing condensed milk for freezing: pasteurize at 180° F. for 15 minutes, condense to a concentration of 3:1 in a stainless steel vacuum pan, homogenize at a pressure of 3000 pounds per square inch, cool to 40° F., freeze initially in an ice cream freezer, and package and complete the freezing at − 15 to − 20° F. When concentrated milk is held in frozen storage, protein destabilization occurs and this may proceed to substantial flocculation of the protein. Milk exposed to high or extended heat treatment before being condensed and frozen shows a greater tendency to protein destabilization than milk heated to a less extent. Bell [10] also finds that market milk may be preserved satisfactorily in the form of homogenized frozen condensed milk for two to four weeks.

Sterilized fluid milk has not been manufactured to any extent in the United States, but a sterilized cream is now being produced and marketed. Webb [119] describes a process for producing sterilized cream. Fresh cream of low titratable acidity (0.15 per cent or less as lactic acid) is standardized to 20 per cent fat, preheated to 176° F. without holding, and double-homogenized at this temperature at 2500–3000 and 500 pounds pressure per square inch. The cream is then cooled to 60° F., filled into cans, and sterilized as for evaporated milk.

Avoset is a type of commercially produced sterilized cream product containing a vegetable stabilizer. This product, made in two grades of 18 and 30 per cent fat, is sterilized in a continuous flow heating unit, known as the Grindrod process.[43, 44]

Dried Milk

Nonfat milk solids or defatted milk solids is the proper name assigned by Act of Congress (Public Law 244, 78th Congress) to the dry product obtained by removing substantially all the fat and all the water from whole milk. The development and economic status of the industry are given by Beardslee [8] and by Cook and Day,[13] and an excellent technical discussion of the dried milk industry is given by Hunziker.[58]

Dried milks have been of interest to man for hundreds of years. Marco Polo in 1295 reported that the soldiers of the Mongol Emperor Kublai Khan carried with them in their wars a milk prepared by drying a milk paste in the sun. The various products of milk which are now available in dried form are dried whole milk, dried nonfat milk, dried cream, dried buttermilk, dried whey, dried ice cream mix, dried malted milk, and dried sweetened condensed milk. Of these products dried nonfat solids are produced in the largest quantity: 658,515,000 pounds in 1948. The war gave great impetus to the production of dried milks and to improvement in their quality, since dried milks represented the most concentrated form in which this important food product could be provided for the armed forces.

The three processes used in the manufacture of nonfat milk solids are: the spray, the vacuum-roller, and the roller process. These processes are shown diagrammatically in Figure 1. It is to be noted that the vacuum-roller process merely involves conducting the roller drying in a vacuum chamber. Actually only very small quantities of dried milk are produced by the vacuum-roller process.

TABLE 48. SPECIFICATIONS FOR STANDARD AND EXTRA-GRADE NONFAT DRY MILK SOLIDS

	Process		
Standard-Grade	Spray: Not Greater than	Vacuum Drum: Not Greater than	Atmospheric Roller: Not Greater than
Butterfat, %	1.50	1.50	1.50
Moisture, %	5.00	5.00	5.00
Titratable acidity, [1] %	0.17	0.17	0.17
Solubility index [1,2] ml.	2.00	5.00	15.00
Bacterial estimate, per g.	300,000	300,000	300,000
Sediment, [1]	No. 4	No. 4	No. 4
Extra-Grade			
Butterfat, %	1.25	1.25	1.25
Moisture, %	4.00	4.00	4.00
Titratable acidity, [1] %	0.15	0.15	0.15
Solubility index, [1,2] ml.	1.25	2.00	15.00
Bacterial estimate, per g.	100,000	100,000	100,000
Sediment, [1]	No. 3	No. 3	No. 3

[1] Determination made on reliquefied sample.

[2] Solubility index is a measure of the insoluble residue which is higher, the higher the index.

In the roller drying of milk, the fluid product is applied to the smooth surface of continuously rotating steam-heated drums or rollers where the moisture is evaporated, leaving a film of dry milk which is shaved off by a knife. The sheet of dried milk is then ground and packed in proper containers. Combs and Hubbard[12] have showed that an increase in steam pressure, which permits greater drum speed, heating the milk going to the dryer, and simultaneous increase of drum speed and of steam pressure increase the capacity of the dryer.

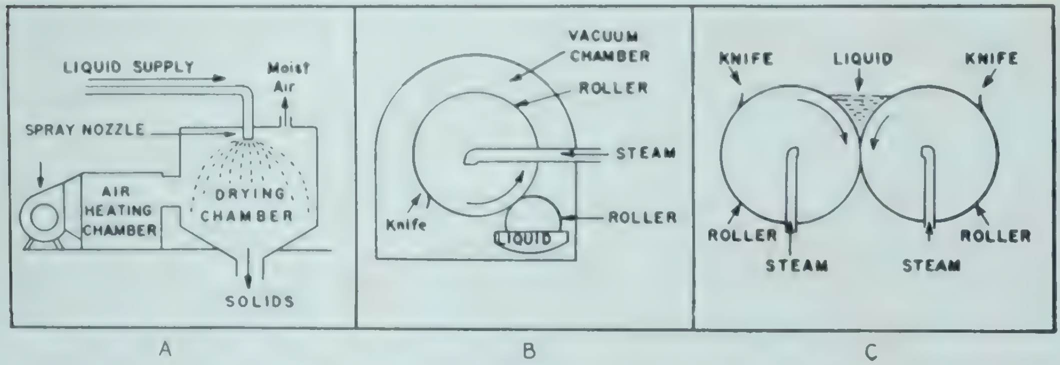
LIQUID SUPPLY
Moist Air
SPRAY NOZZLE
AIR HEATING CHAMBER
DRYING CHAMBER
SOLIDS
VACUUM CHAMBER
ROLLER
STEAM
Knife
ROLLER
LIQUID
KNIFE
LIQUID
KNIFE
ROLLER
ROLLER
STEAM
STEAM
A
B
C

FIG. 1. (a) Spray drier. (b) Vacuum roller drier. (c) Roller drier. Schematic presentation of milk drying process.

In the drying of milk by the spray process, milk previously concentrated in a vacuum pan or concentrated in a unit of the spray-drying process is atomized in a hot air chamber. The concentrated milk with 30 to 40 per cent total solids may be atomized by pressure through a spray nozzle, or it may be atomized by centrifugal wheels operating at a high peripheral speed. Hunziker [58] describes in detail the several roller and spray-drying systems in industrial use.

Dried Nonfat Milk. Standards for nonfat milk solids have been established by members of the dry milk industry, and a grading booklet [3] has been published, giving grades and methods of conducting the chemical and other tests on the product, as well as general requirements for nonfat milk solids. In addition, extra grade of nonfat milk solids is so designated as to indicate the highest quality of nonfat dry milk solids and, along with the foregoing general requirements, must meet specifications as shown in Table 48.

TABLE 49. RELATION BETWEEN MILK SOLIDS CONCENTRATION AND TIME OF HEATING AT 100° C. REQUIRED TO INDUCE 50 PER CENT INSOLUBILITY

Milk Solids Concentration %	Time of Heating Required
8	7 1/2 hours
18	2 hours
28	33 min.
38	8 min.
48	2 min.
58	31 sec.
68	8 sec.
78	2 sec.
88	0.4 sec.

It will be noted that the method of manufacturing the powder affects the magnitude of the solubility index. Wright [127] has shown the relationship of the total solids content at which milk is heated to the protein which becomes insoluble under that condition of heating. The data of Wright are given in Table 49. This reaction is responsible for the heat insolubilization which occurs when milk is dried by the roller process. With exposure to lower temperature as when dried by the vacuum-roller process, there is less protein rendered insoluble. In the case of spray drying where the atomized milk particles are kept cooler during drying by evaporation of water, still less protein is rendered insoluble. For spray-dried milk, vacuum-roller-dried, and roller-dried milks, the solubility indices are 1.25, 2.00, and 15.00 ml., respectively.

O'Malley and Baldi [76] have analyzed 32 samples of nonfat milk solids obtained from the production of various states and at different seasons of the year. Their data give results not usually obtained in the grading of nonfat solids and are summarized in Table 50. Average data for some of the other vitamins in nonfat milk solids show the following values in terms of micrograms per gram: 8.5 of niacin, 0.30 of biotin, 4.5 of pyridoxine, 53.5 of pantothenic acid, 0.05 of folic acid, and 600 of inositol.

TABLE 50. CHEMICAL COMPOSITION OF NONFAT MILK SOLIDS

	Moisture %	Fat %	Protein [Nx6.38]%	Lactose %	Ash %	Calcium	Phosphorus	Riboflavin γ per g.	Thiamine γ per g.
Mean of all samples	3.46	0.81	35.45	51.34	8.03	1.31	1.02	19.18	3.85
Maximum of all samples	3.90	1.24	37.90	53.80	8.34	1.40	1.07	21.23	3.80
Minimum of all samples	2.50	0.47	33.79	47.80	7.67	1.26	0.97	20.93	3.57

Large quantities of nonfat solids are used in the baking industry, and this has required a specially processed product.[4] Grewe and Holm [42] found that preheating milk had a marked effect on its baking quality and it is now common practice to preheat milk at 185° F. for 15 minutes or some equivalent heat treatment in preparing it for bakery purposes. A laboratory baking test is largely used in testing milk for baking quality, but recently the determination of whey protein nitrogen by the Harland and Ashworth [48] method or the Farinograph method of Hoffman et al.[54] has been used for this purpose.

Dried nonfat solids are very hygroscopic. The product must accordingly be packaged in containers which will not permit absorption of moisture. Dried milk solids which attain a moisture content above 4 per cent are subject to caking, develop a brown coloration, and the protein may become insolubilized. Supplee [109] and Henry et al.[51] have studied humidity equilibria and moisture contents of dried milks and the changes which take place as a result of eventual increased moisture content of dried milk products.

Skim milk powder is the dried separated milk which is prepared for animal feed. Production of this product in 1948 was 14,020,000 pounds. Feed grades for dried milk provide that the product be made from freshly skimmed milk to which no preservative, alkali, or other neutralizing agent has been added and which has been pasteurized either before or during the drying process at 145° F. for 30 minutes or its equivalent in bacterial destruction. Dry skim milk for animal feed is classified into three grades:[1] choice feed grade, standard feed grade, and sample feed grade.

Dried Whole Milk. Dried whole milk may be prepared by the same processes and the same equipment as for nonfat milk solids. Estimated production for 1948 was 172,980,000 pounds, equivalent to the drying of about 1,441,500,000 pounds of fluid milk. A bulletin [2] on the grading of dry whole milk and sanitary and quality standards, including standard methods of analysis, gives the specific grading requirements for dried whole milks as shown in Table 51. An average analysis of dry whole milk is the following: 2 per cent moisture, 27 per cent fat, 26.50 per cent protein, 38.0 per cent lactose, and 6.05 per cent ash.

TABLE 51. SPECIFIC GRADING REQUIREMENTS FOR DRY WHOLE MILK

		Gas Packed, Spray Process	
		Premium	Extra
Butterfat	Not less than	26.00 %	26.00 %
Moisture	Not more than	2.25 %	2.50 %
Titratable Acidity[1]		0.15 %	0.15 %
Bact. Estimate		50,000 per gm.	50,000 per gm.
Sol. Index[1]		0.50 ml.	0.50 ml.
Sediment		No. 2	No. 3
Flavor-Odor[1]		Normal	Normal
Color		Normal	Normal
Copper		1.5 ppm	1.5 ppm
Iron		10.0 ppm	10.0 ppm
Oxygen		2.0 %[2]	3.0 %[2]

		Bulk, Spray Process	
		Extra	Standard
Butterfat	Not less than	26.00 %	26.00 %
Moisture	Not more than	2.50 %	3.50 %
Titratable Acidity[1]		0.15 %	0.17 %
Bact. Estimate		50,000 per gm.	125,000 per gm.
Sol. Index[1]		0.50 ml.	1.0 ml.
Sediment[1]		No. 3	No. 4
Flavor-Odor[1]		Normal	Normal
Color		Normal	Normal
Copper		1.5 ppm	3.0 ppm
Iron		10.0 ppm	15.0 ppm

		Bulk, Roller Process	
		Extra	Standard
Butterfat	Not less than	26.00 %	26.00 %
Moisture	Not more than	3.00 %	5.00 %
Titratable Acidity[1]		0.15 %	0.17 %
Bact. Estimate		50,000 per gm.	125,000 per gm.
Sol. Index[1]		15.0 ml.	15.0 ml.
Sediment[1]		No. 3	No. 4
Flavor-Odor[1]		Normal	Normal
Color		Normal	Normal
Copper		1.5 ppm	3.0 ppm

[1] Determination made upon reliquefied sample.

[2] Calculated to atmospheric pressure. This determination is to be made 7–10 days after final gas packaging.

The milk fat which is associated with dried whole milk brings with it problems of keeping quality. Hydrolyses by milk and bacterial enzymes and autoxidation catalyzed by air, light, heat, acidity, such metallic ions as copper and iron, and pro-oxidant substances in the milk are all involved. Factors which result in the production of a dried whole milk of improved keeping quality are use of high quality fresh milk, clarification and homogenization of the milk, preheating to 185° F. and holding the milk for 30 minutes, or some comparable heat treatment, and prompt removal from the drying chamber. Coulter[14] has shown that reducing substances which have antioxidant value are produced by the heat treatment.

Factors which are concerned with the keeping quality of dried whole milk may or may not involve oxidation. In order to prevent fat oxidation in dry whole milk, gas packing of the product has become common practice. In the premium-grade product the headspace gas may not contain over 2 per cent oxygen. Shipstead and Brant [102] report the application of gas packing to whole-milk powder and the improvements in keeping quality derived therefrom. Gas packing is accomplished by removing the air by evacuation and then replacing the air with nitrogen or a mixture of 80 per cent nitrogen and 20 per cent carbon dioxide. In order to obtain more complete removal of the oxygen, double gas treatment with an interval between the treatments to permit liberation of sorbed oxygen is sometimes accorded dried whole-milk powder. Dried milk powder releases sorbed oxygen slowly, hence the reason for the grading specification that oxygen content be determined 7 to 10 days after gas packing so as to be certain that the oxygen found represents the final equilibrium condition.

Coulter, Jenness, and Crowe [16] designate the following nonlipid changes which occur in dried whole milk during storage: a stale or burnt feathers flavor, production of ferricyanide and indophenol reducing substances, production of carbon dioxide, utilization of oxygen, production of water, production of extractable fluorescent materials, browning, loss of lactose, increase of acidity, and loss in solubility. All these changes increase in rate with increase in moisture content and temperature. The importance of maintaining the moisture level at the specified standard of 2 per cent is accordingly indicated.

Spray-dried and roller-dried whole milk powders are quite different in their physical characteristics, due primarily to factors having to do with the difference in solubility index of the two products. Spray-dried powder is indicated where completeness of dispersibility is desirable as, for example, for reconstituting for beverage purposes. The roller-process product may be used where dispersibility is not a significant factor as in the baking or the milk chocolate industries.

Bacterial standards are given for dry milk products in the specifications. The bacterial content of dried milks undergoes no change at all during storage or it may show a decrease.

Miscellaneous Dried Milk Products. Dried cream is manufactured only by the spray process. The same problems and precautions exist in the making of dried cream as for dried whole milk. Dried creams of 50, 65, and 72 per cent are manufactured. The moisture standard for a dried cream of 50 per cent fat content is 1.0 per cent with correspondingly lower moisture contents for dried creams of higher fat contents. The percentage composition of a dried cream at the high level of fat content is 71.15 per cent fat, 11.12 per cent protein, 14.74 per cent lactose, 2.43 per cent ash, and 0.55 per cent moisture. The production of dried cream in the United States in 1947 was 320,000 pounds.

The manufacture of dry ice cream mix was given great importance during the war period and even in 1946 the production of this product was 17,429,000 pounds. The United States Quartermaster Corps specifies a product of not less than 27 per cent fat, not less than 27.5 per cent solids-not-fat, not less than 39.5 per cent sugar, and not more than 1.0 per cent stabilizer and unspecified 2.75 per cent. The same precautions must be observed in processing dried ice cream mix as for dried whole milk. Usual practice is to add about 25 per cent of the sugar to the standardized ice cream mix before drying with the remainder added to the dried mix. Tracy [112] describes the manufacture of dried ice cream mix. Dried ice cream of the composition given is prepared for freezing by the addition of 7.3 pounds of water per 4.25 pounds of the product.

Dehydrated sweetened condensed milk is prepared as follows: milk of standardized fat and solids not fat content is preheated to 180–200° F., sugar added and the mixture concentrated under vacuum at 125–145° F. to a total solids content of 36 to 42 per cent. The condensed product is then spray dried to yield the dehydrated product containing 12.5 per cent milk fat, 25 per cent sucrose, and 3.25 per cent moisture and the balance nonfat milk solids. This product has excellent keeping quality even without gas packing. It has found use as a sweetened milk in coffee and in manufactured products.

Malted milk is made by combining whole milk with the clear liquid from a ground barley malt and whole-wheat flour mash. Crushed barley malt is steeped in water at about 90° F. for 30 minutes to permit release of the enzymes. The whole-wheat flour is prepared for the action of the malt by cooking the mixture of whole-wheat flour and water (1:1.3 ratio) at 200° F. for 2 hours. A digestion mixture of 1 part of the flour to 2.5 parts of barley is then prepared and the digestion allowed to proceed until starches are converted to dextrins and maltose and the cereal proteins are converted to soluble nitrogenous compounds. At the end of digestion the clear liquid is drawn off and the washings from the fibrous hulls and precipitate combined with the extract. The extract containing about 11 per cent of solids is combined with whole milk and standardized. Salt (0.75 pound per 100 pounds of the malt–flour mixture) and soda to neutralize the acidity are then added and the mixture pasteurized and condensed to 68–70 per cent solids. The concentrated syrup obtained is then discharged for drying in a drum dryer or in a spray dryer or in a special vacuum pan, the latter being preferred. When the removal of water in the vacuum pan has reached a certain point, air is admitted, dropping the vacuum to 15 inches. The continued action of an agitator disperses air throughout the semisolid mass. On completion of aeration, the vacuum is suddenly raised to 27.5 inches causing the entrained air to expand and the mass to rise forming a solid mass of porous product. The final product is then removed in blocks or broken up, depending on the use to which it is to be put. Malted milk is hygroscopic, but when properly protected from moisture absorption the product has very good keeping quality. Malted milk may be marketed plain or flavored with chocolate.

United States Federal Standards provide that malted milk shall contain not less than 7.5 per cent milk fat and not more than 3.5 per cent moisture. An average analysis of plain malted shows 2 per cent moisture, 8.40 per cent fat, 71.72 per cent carbohydrate, 13.44 per cent protein, 0.27 per cent fiber, and 4.01 per cent ash. For chocolate malted milks these data are 2.24 per cent moisture, 5.41 per cent fat, 79.19 per cent carbohydrate, 10.04 per cent protein, 0.29 per cent fiber, and 2.84 per cent ash.

Buttermilk available from butter making may be converted into a dry product and in 1948, 41,720,000 pounds of dry buttermilk were manufactured. Buttermilk obtained from the churning of sweet cream may be dried in the same manner as nonfat milk solids. An average composition of such a product is the following: 3.31 per cent moisture, 33.79 per cent protein, 5.54 per cent fat, 47.86 per cent lactose, 8.29 per cent ash, and 1.21 per cent acidity as lactic acid. A large proportion of dried buttermilk made in this country is made from acid buttermilk. The food grade of dry buttermilk powder is usually standardized in acid content. The representative composition of such a product is the following: 1.98 per cent moisture, 38.74 per cent protein, 5.87 per cent fat, 39.91 per cent lactose, 7.68 per cent ash, and 5.87 per cent acidity as lactic acid. Sweet cream buttermilk finds special use in the chocolate candy, baking, and ice cream industries, while the acid buttermilk powder is used as a constituent of dark cakes and of rye bread.

The acidity of acid types of buttermilk causes difficulty in drying as the product tends to form sticky masses on the roll and to be sticky when dried, often caking and browning. These difficulties are overcome to some extent by neutralizing or partially neutralizing the buttermilk before drying. Collis[11] describes a method for drying acid buttermilk. Buttermilk handled in the proper manner is a satisfactory food product, but much dried buttermilk finds its way into animal feed products.

Whey contains about 70 per cent of its solids as lactose and this introduces special difficulties in drying the product. Supplee[108] and Jack and Wasson[61] have attempted to eliminate the so-called melassegenic properties of whey by the addition of cereal or diatomaceous material to the whey before drying by the roller process.

Whey may also be dried by the spray process but when so dried it is very hygroscopic. To obviate this hygroscopicity, Peebles and Manning[80] have modified the spray drying process to permit change from the hygroscopic form of lactose to the nonhygroscopic form. Whey is first heated to 200° F. and concentrated to 45–60 per cent solids. This concentrate is then sprayed into a dryer to yield a product of 12 to 15 per cent moisture. Effort is made to control the temperature so that the lactose will be converted into the monohydrate form and crystallization will take place with the simultaneous removal of water. On removal from the drying chamber the partially dried material is fed to a conventional heated rotary drier where the remainder of the moisture is removed. A nonhygroscopic free-flowing dried whey is obtained by this process. Lavett[67] describes a two-stage roller dryer that produces dried whey of similar properties. Simmons[103] has developed another process for drying whey. The whey is concentrated to 70 per cent solids, the concentrate dropped into crystallizing tanks where it is cooled and seeded with α-lactose crystals. After the crystallization the mass is broken up and dried with hot air to yield a nonhygroscopic type of dried whey.

The production of dried whey in the United States in 1947 was 157,583,000 pounds which product was largely used in animal feeds. Dried whey has an average analysis of 6.10 per cent moisture, 0.90 per cent fat, 12.56 per cent protein, 72.25 per cent lactose, and 8.90 per cent ash. Webb and Whittier[121] review uses for whey in food, feed, and industry.

Drying of organic matter from the frozen condition, under high vacuum, has been known for a long time and several methods involving low temperatures have been applied to concentrating and drying milk. Ice formed on the surface of milk on freezing may be broken periodically during formation so that eventually the milk becomes a snowlike mass with almost pure water existing in the frozen crystals. Centrifugation operates to remove the ice crystals, and the concentrated milk is allowed to freeze in a thin layer on a rotating refrigerated disc. The frozen concentrate of milk solids can then be scraped from the rotating disc in the form of flakes which are dried in a vacuum oven or with moderate heat. Irvin[60] also describes a method of removing water from frozen milk by using silica gel to remove the water vapor.

The Chain Belt Company of Milwaukee has attempted to adapt freeze drying to milk. A vacuum drying chamber designed to operate at 0.5 mm. absolute pressure, a suitable vacuum pump for initially removing practically all the air, a chamber with means of applying heat to the frozen evaporating milk as it passes through the chamber on a movable belt, and equipment for regenerating a solution of lithium chloride solution constitutes the process. The milk to be dried is sprayed on the movable belt where it freezes. The belt then moves the frozen milk to heating plates which supply heat which sublimates the water in the frozen milk, the water vapor generated being absorbed in the lithium chloride solution. The dry product then passes through an air lock where it is collected in an atmosphere of nitrogen. Another development along this line is being pioneered by National Research Corporation of Cambridge, Massachusetts, and no doubt others are working on such a process. However, no processes of this type are in commercial operation.

Ice Creams

The preparation of the ice cream mix is the first step in the manufacture of ice cream. The mix may consist of a considerable variety of ingredients, all selected and standardized so that the final mix composition and the eventual ice cream composition will meet the required standards. The properties of the dairy products commonly used in the mix have been discussed in the preceding sections of this chapter. Thus, in making the ice cream mix the various ingredients, except the flavoring material, are mixed, pasteurized, and homogenized together. A common pasteurizing procedure is to heat to 150–160° F. and hold for 30 minutes. All commercial ice cream mixes are homogenized. The benefits to be derived from this process are better whipping ability of the mix, better body and texture of the finished ice cream, and elimination of the dangers of churning during freezing. Sommer[104] discusses the mechanism of homogenization as applied to ice cream mixes and other effects of such processing on the ice cream and ice cream mix.

Sommer gives the following list of ingredients used in ice cream making.

I. Dairy Products
    1. Milk
    2. Cream
    3. Skim milk
    4. Sweet buttermilk
    5. Plain condensed milk
    6. Plain condensed skim milk
    7. Plain condensed sweet buttermilk
    8. Sweetened condensed milk
    9. Sweetened condensed skim milk
    10. Superheated condensed milk
    11. Evaporated milk
    12. Skim milk powder
    13. Sweet buttermilk powder
    14. Sweet, unsalted butter
    15. Butter oil
    16. Casein
    17. Milk albumin
    18. Malted milk
    19. "Delactosed milk"

II. Sweetening Agents
    1. Cane or beet sugar
    2. Dextrose, glucose, or "corn sugar"
    3. Maple sugar or syrup (used for flavoring)
    4. Invert sugar
    5. Corn syrup, liquid or dried
    6. Honey (used for flavoring)
    7. Malt syrup (used for flavoring)
III. Eggs
    1. Whole egg powder
    2. Powdered egg yolk
    3. Fresh eggs
    4. Frozen eggs
IV. Stabilizers
    1. Gelatin
    2. Sodium alginate (Dariloid)
    3. Gum Tragacanth
    4. India gum
    5. Karaya gum, Indian gum
    6. Locust bean gum
    7. Irish moss
    8. Agar-agar
    9. Pectin
    10. Psyllium seed extract (or ground husks)
    11. Quince seed extract
    12. Sodium-carboxy-methyl-cellulose
    13. Aqualized gums
V. Emulsifiers
    1. Mono- and diglycerides of the fatty acids
    2. Lecithin
    3. Sorbitan monostearate
    4. Polyethylene glycol esters
    5. Polyoxyalkalene of sorbitan monostearate esters
VI. Flavoring
    1. Natural
        a. Vanilla
        b. Cocoa
        c. Chocolate
        d. Cocoanut
        e. Fruits
        f. Fruit extracts
        g. Nuts
        h. Spices

        2. Artificial
            a. Vanilla compounds
            b. Artificial fruit flavors
            c. Imitation maple flavor
            d. Imitation nut flavors
    VII. Colors
        1. Burnt sugar or caramel color
        2. Dyes certified for use in food products
    VIII. Ice Cream "Improvers"
        1. Rennet or pepsin
        2. Commercial improvers depending on enzyme action
        3. Commercial improvers, nonenzymatic

Ice creams differ widely in composition. Table 52 shows the variability of ice cream composition.

TABLE 52. THE COMPOSITION OF ICE CREAM

Constituent	Minimum %	Maximum %	Average Range %	Good %
Fat	8.0	22.0	10 to 12	12.5
Milk-solids-not-fat	6.0+	14.0	10 to 11.5	10.0
Sugar	12.0	18.0	14 to 16	16.0
Stabilizer	0.0	0.7	0.25 to 0.50	0.25 to 0.50
Egg solids	0.0	1.0	0.25 to 0.50	0.50
Na Cl	0.0	0.1		

The various ice cream constituents affect the properties of the ice creams in various ways. The fat increases the richness of flavor, produces smooth textures, and adds body to the ice cream. The nonfat solids improve the texture, help give body, and make possible overrun without snowy or flaky texture. Too high a nonfat solids content permits lactose to crystallize resulting in so-called "sandy" ice cream. Sugar provides sweetness, and improves the texture. Stabilizers absorb water, prevent ice crystallization causing coarse ice cream, and impart smoothness and mouth filling properties to the ice cream. Emulsifiers give a dry-appearing ice cream, small air cell structure, improve the whipping properties, emulsify the fat more satisfactorily, and impart richness to the ice cream.

Ice cream mixes are usually aged before freezing. The improvement in whipping ability is thought to be due in part to the hydration of the stabilizer and the milk proteins and in part to the absorption of materials on the surface of the fat globules. In both hydration and absorption, time and temperature are factors and in the ice cream mix both are favored by low temperatures. In the past the practice was to age ice cream mix for days before freezing but at the present time the aging period is a matter of hours. Dahle, Keith, and McCullough [21] indicate the advisability of aging the mix at least 2 and preferably 4 hours and that in any case 24 hours is sufficient. The aging temperature should be as low as possible without actually freezing the mix.

In the freezing of ice cream mix, the freezing operation accomplishes two objects: the partial freezing of the product and the incorporation of air. The amount of air whipped into the mix is commonly expressed as overrun. Overrun is indicated by the increase in volume over the volume of the original mix expressed as per cent of the volume of the mix. Ice cream mix is frozen by the batch and the continuous process. The whipping properties of ice cream are affected by many factors. The fat content does not have a significant effect on whipping properties; nor does the source of the fat as from butter or cream.[22] The percentage of nonfat solids in the mix within the range used commercially, 8–12 per cent has no pronounced effect on whipping properties but qualitative differences in the nonfat solids do affect whipping properties. Nonfat solids subjected to heat treatment in their preparation improve the whipping properties of ice cream mixes containing them; milks high in calcium salts have a deleterious effect on whipping and are improved by the addition of disodium phosphate, sodium citrate, and sodium caseinate. Increasing the sugar above 13 per cent tends to decrease the whipping properties; stabilizing gums in general tend to limit the whipping properties of mixes but there are exceptions. Egg solids added to ice cream mix improve whipping properties due to the lecithin, whereas fruits and flavors usually impair the whipping properties. Homogenization in such a way as to prevent fat globules clumping improves whipping properties, as does proper aging. The so-called ice cream improvers have an uncertain effect on whipping properties.

The point to which ice cream should be frozen is limited by the consistency of the product. The consistency of the partially frozen and whipped ice cream mix is dependent not only on its freezing point and the amount of water changed to ice but also on the composition of the mix, the overrun and the size of the air cells. With the above limitations in mind, it may be stated that the temperature at which the ice cream is drawn from the freezer varies between 21 and 25° F. As the water separates out as ice crystals the remaining portions become more concentrated and the viscosity increases. It is the usual practice to draw the mix from the freezer at the maximum viscosity that it can be handled, after which it passes into containers and then to the hardening room. The hardening room is maintained at temperature from 0 to − 20° F. and here the freezing of the ice cream is continued. This completes the manufacture of the product.

Flavor, body, and texture are the principal factors used in judging the quality of the finished ice cream. Flavor is a function of high quality ingredients and their proper combination in the ice cream. The body of ice cream is related to the mass as a whole, its consistency or firmness and resistance to melting. The texture is related to the size, shape, and arrangement of the small particles. Sommer discusses the effects of ice cream composition and processing on body and texture characteristics. Snyder[105] finds such emulsifiers as lecithin, mono- and diglycerides, sorbitan monostearate, and the polyoxyalkylene derivatives of sorbitan monostearate to be useful in ice cream.

Ices and sherberts are manufactured in a manner similar to ice cream. Dahlberg[18] defines ices and sherberts as follows: ''A water ice is a semifrozen product made of water, sugar, and fruit juice which may or may not contain added color, flavor, fruit acid, and stabilizer.''

A sherbert is a semifrozen product made of the same ingredients as water ice except that it also contains milk or milk products. The acids used in ices are citric, tartaric, and lactic. The acidity expressed as lactic acid is usually about 0.35 per cent. Basic ice and sherbert mixes are the following:

	Basic Ice Mix	*Basic Sherbert Mix*
Sucrose	21.0	20.0
Dextrose or invert sugar	9.0	8.0
Pectin	0.25	0.22
Gelatin	0.25	0.22
Water	49.5	41.56
Ice cream mix	—	10.00
Flavor (fruit juices, etc.)	20.00	20.00
Total	100.0	100.0

Ice and sherbert mixes are frozen in the same manner as ice cream mixes, but to a considerably lower overrun (25 to 40 per cent for ices and sherberts). Because of the somewhat greater amount of water in ices and sherberts than in ice cream, stabilizers are more important. The stabilizers in common use are gelatin, gum tragacanth, India gums, agar-agar, and pectin. Dahlberg[17] discusses the advantages of various combinations of gum and gelatin. Pectin has come into extensive use as a stabilizer because of its gel-forming properties in acid solution.

Combinations of sucrose and dextrose or invert sugar are used in ices and sherberts in order to prevent the development of the crusty spots on the surface of these products containing only sucrose.

The ice cream-making procedure can, of course, be applied to a great many combinations of ingredients. ''Ice milk'' or milk ice generally contains 4 per cent fat, 12 to 14 per cent nonfat milk solids and is similar to ice cream in sugar, stabilizer, emulsifier, and overrun. Frozen custards are ice cream-like products containing eggs; in Wisconsin this product must contain not less than 5 egg yolks or their equivalent per gallon of the product. Sommer and Turnbow and Raffetto [115] give directions for making many ice cream novelties and specialties.

DAIRY BY-PRODUCTS

Casein. Acid casein is manufactured by heating skim milk to 34 to 40° C. and acidifying to the isoelectric range of pH 4.1 to 5.5. The precipitating acid may be lactic, sulfuric, or hydrochloric. Lactic acid may be used as such or may be added to the skim milk as sour whey or may be caused to develop in the skim milk by the use of starter (self-sour process). In the making of rennet casein, commercial rennet extract containing the coagulating enzyme, rennin, is used to effect coagulation of the casein in the skim milk. The casein curd obtained either by acid or rennin coagulation is removed from the whey by decantation or by passing over a false bottom trough and is then washed thoroughly to remove acid, milk sugar, salts, and other whey constituents. The washed curd is pressed to remove as much water as possible and then ground to facilitate drying in a tunnel drier. The dried casein is finally ground to the desired particle size, for example to 24, 30, 60, or 80 mesh. From 2.2 to 2.8 pounds of dried casein are usually obtained from 100 pounds of skim milk. The casein obtained by rennet coagulation has an ash content of not less than 7.5 per cent while acid-precipitated casein may not have an ash content of more than 4 per cent.

Lactose. Lactose may be prepared from casein whey or from cheese whey. Whey assembled in large tanks is heated with direct steam and neutralized with lime to pH of 6.2. The heating coagulates the albumin so that the clear deproteinated whey can be drawn off and concentrated. The concentrated syrup (30 per cent solids) is passed through a filter press to remove additional coagulated protein and the concentration continued to a density of 40° Bé. The hot mass is then dropped to crystallizing vats where cooling and crystallization takes place during the course of several days, after which the wet mass is taken to sugar centrifuges. The wet crude lactose (yellow in color) should be refined at once or dried to prevent decomposition. For refining, the crude sugar is dissolved in 30 per cent concentration and 0.25 per cent filter aid plus 1 pound of decolorizing carbon added per 100 pounds of lactose. The batch is heated to boiling and made to 0.09 per cent acid concentration with HCl and allowed to stand overnight to permit maximum decolorization. Thereafter the batch is heated to boiling, neutralized to pH 5.4–5.8, boiled vigorously, and allowed to stand for sedimentation, after which the clear liquid is passed through the filter press. This liquid is then concentrated and lactose allowed to crystallize as previously described. The refined lactose crystals are then dried and ground. By proper recovery of filtrates from the sludge and the wash waters from the crude and refined lactose crystals, 60 per cent of the lactose contained in the original whey may be recovered.

The refined lactose of commerce is a white odorless powder consisting of crystals which have been ground to pass a 100-mesh screen. The product is 99.7 per cent pure as determined by polariscope and contains not more than 0.50 per cent ash and not more than 0.02 per cent nitrogen or fat. It yields a clear, colorless, odorless, neutral solution. Herrington[52] states that the crystal habit of lactose varies greatly under different conditions of crystallization, the principal factor governing the crystal's growth habit being the precipitation pressure, the ratio of the actual concentration to the solubility. In commenting on the structure of lactose crystals, Hunziker and Nissen[53] state that lactose crystals belong to Class C_2. They are monoclinic sphenoidal and have only one axis of symmetry with trapezoidal side faces and rhombic tops and bottoms. Fully developed crystals have, in addition, beveled faces at the base and apex which may terminate in a sharp edge, giving the crystal a tomahawk appearance.

Hydrolyzed lactose syrup may be prepared by treating lactose with lactase or by hydrolyzing with acid. Ramsdell and Webb[87] report that 93 per cent of the theoretical yield of glucose and galactose were obtained on the hydrolysis of a 30 per cent lactose solution, using 0.007 molecule of hydrochloric acid per 1000 g. of the mixture and heating to 147° C. during a 65-minute heat treatment. Turnbow[114] describes the process of manufacturing a food product such as ice cream using skim milk treated with a lactose-inverting enzyme.

Whittier[123] discusses details of lactose manufacture and the uses of lactose in dietary and pharmaceutical products, as well as the use of lactose in terms of its hydrolytic, pyrolytic, oxidation, hydrogenation, substitution, and fermentation products.

Lactic Acid. Several industrial fermentations are being conducted on whey remaining from cheese and casein production. Whittier and Rogers[124] describe the production of lactic acid by fermenting the lactose in whey by a mixture of a lactobacillus and a mycoderm. Burton[10a] describes the commercial production of lactic acid and lactate salts. Whey neutralized to pH 6.5–7.5 with calcium oxide or calcium carbonate is inoculated with the lactic acid-producing organisms. The whey is then heated to about 110° F. and additional quantities of the calcium carbonate and calcium oxide added during fermentation so that the pH is held between 5.5 and 7.0. Temperature and pH are held at an optimum so that lactose fermentation will proceed as rapidly as possible (usually during 42 to 48 hours). At the end of fermentation, the batch is neutralized with lime and heated to about 205° F. to coagulate the protein and permit its removal by sedimentation. The precipitate after washing is dried and used as animal feed. The clear liquid and washings are combined and treated with decolorizing carbon and concentrated in a vacuum pan to 15° Baumé. The concentrated solution of calcium lactate is then placed in cold water-jacketed crystallizing vats. The calcium lactate that crystallizes after 10–12 hours is removed by centrifuging and the crystals washed with cold water. The crystals are then dissolved in water at 150° F. and decolorizing carbon and filter aid added. The solution is filtered, concentrated, cooled and crystallization allowed to proceed as described. By repeating this operation calcium lactate of various degrees of purity may be obtained, including a U.S.P. grade. The mother liquor and the wash waters obtained along the process are used for the recovery of additional calcium lactate.

The calcium lactate produced by this process has the formula $Ca\ (CH_3CHOHCOO)_2 \cdot 5H_2O$. Casein whey containing about 4.6 per cent of lactose should yield theoretically 7.8 pounds of calcium lactate per 100 pounds of whey. This process of preparing calcium lactate is also described by Johnson et al.,[63] and by Weisberg et al.[122]

By use of salts other than calcium, other lactates can be prepared by this process. Sodium lactate syrup of 50 per cent concentration is obtained when neutralization is with sodium carbonate.

Lactic acid may be prepared from the calcium lactate by reaction with sulfuric acid to yield lactic acid plus insoluble calcium sulfate.

Ethyl alcohol may be manufactured by fermenting the lactose in whey. Myers and Weisberg [73] describe a process by which whey is first pasteurized and then inoculated with a vigorous culture of *Saccharomyces fragilis.* Fermentation at 25 to 30° F. proceeds until all the lactose has been consumed. Vigorous aeration during the fermentation is necessary to remove carbon dioxide which, if present, would retard the fermentation. The residual matter after removal of the alcohol is a valuable food product, constituting a concentrate of vitamins, milk salts, whey proteins, and protein elaborated by the yeast.

Rogosa, Browne and Whittier [96] report a method for producing alcohol from whey using *Torula cremoris* as the organism to ferment the lactose. Kauffmann and Van der Lee [64] obtained alcohol from whey by use of an organism obtained from Gervais cheese.

Pollard, Rodgers and Meade [82] describes a procedure for increasing the riboflavin content of fermented whey or skim milk. The whey or milk at pH 6–7 is sterilized by heating at 250° F. for 10–20 minutes. Calcium carbonate may be added to enhance riboflavin production and the iron adjusted to 0.5–4.5 p.p.m. The media is brought to 100° F. and inoculated with *Clostrodium acetobutylicum.* After fermentation for 12 to 48 hours under these conditions the riboflavin content of the whey may be increased from 1.4 to 70 γ per ml. in the fluid whey, corresponding to an increase of from 240 to 2800 γ per g. on the dry basis. Supplementing whey with a zinc content of 0.15 to 3.5 p.p.m. as well as supplementing with magnesium and manganese also enhances riboflavin production. Solvents such as acetone and *n*-butyl alcohol are also produced by the organisms and recovered by distillation.

Normal butyl alcohol an acetone are produced by another type of whey fermentation as described by Frey, Gluck, and Oehme.[36] This operation is conducted in the following manner: the whey is heated to 84–90° C. care being taken that shortly before the beginning of protein precipitation the temperature is increased slowly; at the precipitation temperature air, nitrogen or other gas is forced in small bubbles through the whey to prevent large flocks of curdled whey from formin. On completion of the precipitation, the whey is neutralized. With an acid value of 1.09 ml. of 1 N sodium hydroxide per 20 ml., about 2.2 kg. of dry calcium hydroxide is added per cubic meter in order to set up the proper acidity for fermentation (0.06 per cent as lactic acid). The whey is then inoculated with *n*-butyl alcohol-producing bacteria and during a 48-hour fermentation the lactose is practically entirely removed. About 90 per cent of the lactose appears as *n*-butyl alcohol and acetone. One cubic meter of whey yields 3.2 kg. of acetone and 15.8 kg. of *n*-butyl alcohol.

The production of by-products from milk has by no means been completely explored. Further research in this field will undoubtedly result in many new products of economic importance.

BIBLIOGRAPHY

1. American Dry Milk Institute, "Feed Grades for Dry Skim Milk." Chicago, Ill. (1944).
2. American Dry Milk Institute, "The Grading of Dry Whole Milk and Sanitary and Quality Standards Including Standard Methods of Analysis." Chicago, Ill. (1947).
3. American Dry Milk Institute, "The Grading of Non-Fat-Milk-Solids and Sanitary Quality Standards." Chicago, Ill. (1948).
4. American Dry Milk Institute, *Bull. No.* **100**. Chicago, Ill. (1947).
5. Association of Official Agricultural Chemists, "Methods of Analysis." 6th ed. Washington, D. C. (1945).
6. Babcock, C. J., Stabile, J. N., Windham, E. S., and Randall, R., *J. Dairy Sci.* **32**: 175 (1949).
7. Babcock, S. M., in Leach and Winton "Food Inspection and Analysis," pp. 111. New York, John Wiley and Sons, Inc. (1920).
8. Beardslee, C. E., "Dry Milk, The Story of Our Industry." American Dry Milk Institute, Chicago, Ill. (1948).
9. Bell, R. W., *J. Biol. Chem.* **64**: 391 (1925).
10. Bell, R. W., *J. Dairy Sci.* **22**: 89 (1939).

10a. Burton, L. V., *Food Ind.* **9**: 571, 617 (1937).

11. Collis, N. P., U. S. Pat. 1,377,777 (October 7, 1919); U. S. Pat. 1,356,340 (October 19, 1920).
12. Combs, W. B., and Hubbard, E. F., *J. Dairy Sci.* **15**: 147 (1932).
13. Cook, H. L., and Day, G. H., "The Dry Milk Industry." American Dry Milk Institute, Chicago, Ill. (1947).
14. Coulter, S. T., *J. Dairy Sci.* **27**: 607 (1944).
15. Coulter, S. T., *J. Dairy Sci.* **30**: 995 (1947).
16. Coulter, S. T., Jenness, R., and Crowe, L. K., *J. Dairy Sci.* **31**: 986 (1948).
17. Dahlberg, A. C., *J. Dairy Sci.* **10**: 106 (1927).
18. Dahlberg, A. C., *N. Y. Agr. Expt. Sta. Bull.* **536**: 3 (1926).
19. Dahlberg, A. C., and Kosikowsky, F. V., *J. Dairy Sci.* **30**: 165 (1947).
20. Dahlberg, A. C., and Kosikowsky, F. V., *J. Dairy Sci.* **31**: 305 (1948).
21. Dahle, C. D., Keith, J. I., and McCullough, A. D., *Pa. Agr. Expt. Sta. Bull.* **247** (1930).
22. Dahle, C. D., and Josephson, D. V., *Ice Cream Rev.* **19**: 60 (1937).
23. Davies, W. L., "The Chemistry of Milk." New York, D. Van Nostrand Co., Inc. (1936).
24. Davies, W. L., *Proc. 11th World Dairy Congress, Berlin* **2**: 76 (1937).
25. Doan, F. J., and Leeder, J. G., *Food Ind.* **16**: 532 (1944).
26. Doane, C. F., Lawson, H. W., and Matheson, K. J., *U. S. Dept. Agr. Bull.* **608**: 1 (1932, rev.).
27. Dornbush, A. C., Peterson, W. H., and Olson, F. R., *J. Am. Med. Assoc.* **114**: 1748 (1940).
29. *Federal Register* **13**: 6389 (October 30, 1948).
30. Federal Security Agency, Food and Drug Admin., "Standards of Identity for Cheese, Cheese Foods, Cheese Spreads and Related Foods." (21CFB19) (Docket No. FDC46) (February 24, 1947) *Federal Register* **12**(37): 1192–1204 (1947).
31. Fisher, M. H., and Hooker, M. O., "Fats and Fatty Regeneration." New York, John Wiley and Sons, Inc. (1917).
32. Flanigan, G. E., and Supplee, G. C., U. S. Pat. 2,023,014 (December 3, 1935).
33. Fleischmann, Porcher, Ch., and Chevallier, A., *Le Lait* **3**: 17 (1923).
34. "Food Value of Dairy Products." rev. ed. New York, Sealtest (1949).
36. Frey, G., Gluck, H., and Oehme, H., U. S. Pat. 2,166,047 (July 11, 1939).
37. Getz, C. A., Smith, G. F., Tracy, P. F., and Prucha, M. J., *Food Res.* **2**: 409 (1937).
38. Gordon, W. C., Semmett, W. F., and Morris, M., *Federation Proc.* **8**: 202 (1949).
39. Gould, I. A., *J. Dairy Sci.* **22**: 1017 (1939).
40. Greenbank, G. R., *J. Dairy Sci.* **23**: 725 (1940).
41. Greenbank, G. R., *J. Dairy Sci.* **31**: 913 (1948).
42. Grewe, E., and Holm, G. E., *Cereal Chem.* **5**: 461 (1928).
43. Grindrod, G., U. S. Pat. 1,714,597 (May 28, 1939).
44. Grindrod, G., U. S. Pat. 19,193, reissue of Pat. 1,714,597 (June 5, 1934); U. S. Pat. 2,019,491 (November 5, 1935); U. S. Pat. 2,170,195 (August 22, 1939).
45. Hammer, B. W., Horneman, H. C., and Parker, M. E., U. S. Pat. 2,130,643 (September 20, 1938).
46. Hand, D. B., *J. Dairy Sci.* **26**: 7 (1943).
47. Hansen, R. G., and Phillips, P. H., *J. Biol. Chem.* **171**: 223 (1947).
48. Harland, H. A., and Ashworth, U. S., *Food Res.* **12**: 247 (1947).
49. Heath, P. W., U. S. Pat. 1,384,318 (July 12, 1921).

50. Hening, J. C., and Dahlberg, A. C., *N. Y. Agr. Expt. Sta. Tech. Bull.* **197**: 3 (1932).
51. Henry, K. M., Kon, S. K., Lea, C. H., and White, J. C. D., *J. Dairy Res.* **15**: 292 (1948).
52. Herrington, B. L., *J. Dairy Sci.* **17**: 501 (1934).
53. Hilditch, T. P., and Thompson, H. M., *Biochem. J.* **30**: 677 (1936).
54. Hoffman, C., Schweitzer, T. R., Spotts, E. K., and Dalby, G., *Cereal Chem.* **25**: 385 (1948).
55. Holland, E. B., Garvey, M. E., Pierce, H. B., Messer, A. C., Archibald, J. G., and Dunbar, C. O., *J. Agr. Res.* **24**: 365 (1923).
56. Holm, G. E., "Milk Fat and Physical Equilibrium in Milk. Fundamentals of Dairy Science." New York, Reinhold Publishing Corp. (1935).
57. Hunziker, O. F., "The Butter Industry." 3rd ed. Hunziker, La Grange, Ill. (1940).
58. Hunziker, O. F., "Condensed Milk and Milk Powder." 7th ed. Hunziker, La Grange, Ill. (1949).
59. Hunziker, O. F., and Nissen, B. H., *J. Dairy Sci.* **10**: 139 (1927).
60. Irwin, J. C., U. S. Pat. 2,292,447 (August 11, 1942).
61. Jack, E. L., and Wasson, A. J., *J. Dairy Sci.* **24**: 85 (1941).
62. Johnson, A. H., and Ward, F. W., *Cereal Chem.* **13**: 550 (1936).
63. Johnson, A. H., Weisberg, S. M., Johnson, J. J., and Parker, M. E., U. S. Pat. 2,071,346 (February 23, 1937).
64. Kauffmann, W., and van der Lee, P. J., U. S. Pat. 2,183,141 (December 12, 1939).
65. Knight, C. A., Dutcher, R. A., Guerrant, N. B., and Bechdel, S. I., *J. Dairy Sci.* **24**: 567 (1941).
66. Krukovsky, V. N., and Guthrie, E. S., *J. Dairy Sci.* **28**: 565 (1945).
67. Lavett, C. O., U. S. Pat. 2,143,019 (January 10, 1939); U. S. Pat. 2,188,907 (February 6, 1940).
68. Lane-Claypon, J. E., "Milk and Its Hygienic Relations." London, Longmans, Green and Co. (1916).
69. Leach, A. E., and Winton, A. L., "Food Inspection and Analysis." 4th ed. New York, John Wiley and Sons, Inc. (1920).
70. Linderstrom-Lang, K., *Compt. rend. trav. lab. Carlsberg* **17**: No. 9, 116 pp. (1929).
71. McCollum, E. V., Orent-Keiles, E., and Day, H. G., "The Newer Knowledge of Nutrition." New York, The Macmillan Co. (1939).
72. Murray, H. L., U. S. Pat. 2,314,455 (March 23, 1943).
73. Myers, R. P., and Weisberg, S. M., U. S. Pat. 2,128,845 (August 30, 1938).
74. Noll, C. I., and Supplee, G. C., *J. Dairy Sci.* **24**: 993 (1941).
75. North, C. E., U. S. Pat. 158,122; 158,123; 158,124 (May 11, 1926).
76. O'Malley, C. M., and Baldi, E. J., *J. Milk Technol.* **5**: 138 (1942).
77. Orla-Jensen, S., *Le Lait* **3**: 97 (1923).
78. Palmer, L. S., *Missouri Agr. Expt. Sta. Bull.* **163**: 40 (1919).
79. Palmer, L. S., *Am. Coll. Symp. Monog.* **1**: 411 (1923).
80. Peebles, D. D., and Manning, P. D. V., U. S. Pat. 2,181,146 (November 28, 1939).
81. Peterson, M. H., Johnson, M. J., and Price, W. V., *J. Dairy Sci.* **31**: 39, 55 (1948).

82. Pollard, H. L., Rodgers, N. E., and Meade, R. E., U. S. Pat. 2,449,140–44 (September 14, 1948).
83. Polonovski, M., and Lespagnol, A., *Compt. rend.* **192**: 1319 (1931); *Compt. rend. soc. biol.* **101**: 64 (1929).
84. *Pub. Health Serv. Bull.* **220**, rev. to April 1949.
85. Rahn, O., *Kolloid Z.* **30**: 341 (1922).
86. Ramsdell, G. A., and Webb, B. H., *J. Dairy Sci.* **21**: 305 (1938).
87. Ramsdell, G. A., and Webb, B. H., *J. Dairy Sci.* **28**: 677 (1945).
88. Ramsey, R. J., Tracy, P. H., and Ruehe, H. A., *J. Dairy Sci.* **16**: 17 (1933).
89. Rice, F. R., and Markley, A. L., *J. Dairy Sci.* **7**: 468 (1924).
90. Richmond, H. D., "Dairy Chemistry." London, Charles Griffin and Co., Ltd. (1920).
91. Riggs, L. K., U. S. Pat. 2,414,837 (January 28, 1947).
92. Roadhouse, C. L., and Henderson, J. L., "The Market Milk Industry." New York, McGraw-Hill Book Co., Inc. (1941).
93. Rogers, C. E., U. S. Pat. 1,570,646 (January 26, 1926).
94. Rogers, L. A., U. S. Pat. 1,477,153 (December 11, 1923).
95. Rogers, L. A., and associates, "Fundamentals of Dairy Science." New York, Reinhold Publishing Corp. (1935).
96. Rogosa, M., Browne, H. H., and Whittier, E. O., *J. Dairy Sci.* **30**: 263 (1947).
97. Rowland, S. J., *J. Dairy Res.* **9**: 47 (1938).
98. Ruehe, H. A., *Natl. Butter and Cheese J.* **28**, No. 4: 20 (1937).
99. Sammis, J. L., "Cheesemaking." 12th ed. rev. Madison, Wis., Cheese Maker Book Co. (1948).
100. Schrodt and Hansen, *Landw. Versuchst* **31**: 55 (1885).
101. Sharp, P. F., and Hart, R. G., *J. Dairy Sci.* **19**: 683 (1936).
102. Shipstead, H., and Brant, A. P., U. S. Pat. 2,363,445 (November 21, 1944).
103. Simmons, N. L., U. S. Pat. 1,763,633 (June 10, 1930).
104. Sommer, H. H., "Theory and Practice of Ice Cream Making." 5th ed. Madison, Wis. (1946).
105. Snyder, W. E., *Milk Plant Monthly* **38**, No. 6: 30 (1949).
106. Stebnitz, V. C., and Sommer, H. H., *J. Dairy Sci.* **18**: 805 (1935).
107. Storch, C. M., *Le Lait* **3**: 97 (1923).
108. Supplee, G. C., U. S. Pat. 2,173,922 (September 26, 1939).
109. Supplee, G. C., *J. Dairy Sci.* **9**: 50 (1926).
110. Supplee, G. C., and Bellis, B., *J. Biol. Chem.* **48**: 453 (1921).
111. Sutermeister, E., and Browne, F. L., "Casein and Its Industrial Applications." 2nd ed. New York, Reinhold Publishing Corp. (1939).
112. Tracy, P. H., *Ice Cream Trade J.* **41**(4): 22 (1945).
113. Trebler, H. A., U. S. Pat. 2,001,555 (May 14, 1935).
114. Turnbow, G. D., U. S. Pat. 1,737,101 (November 26, 1929).
115. Turnbow, G. D., and Raffetto, L. A., "Ice Cream." New York, John Wiley and Sons, Inc. (1928).
116. Van Slyke, L. L., and Price, W. V., "Cheese." New York, Orange Judd Publishing Co. (1927).
117. Warner, R. C., *J. Am. Chem. Soc.* **66**: 1725 (1944).
118. Webb, B. H., Bell, R. W., Deysher, E. F., and Holm, G. E., *J. Dairy Sci.* **26**: 571 (1943).
119. Webb, B. H., U. S. Pat. 1,646,671 (October 25, 1927).
120. Webb, B. H, and Hufnagel, C. F., *Natl. Butter and Cheese J.* **37**, No. 12: 34 (1946).

121. Webb, B. H., and Whittier, E. O., *J. Dairy Sci.* **31**: 139 (1948).
122. Weisberg, S. M., Chappel, F. L., Stringer, W. E., Stevens, S., and Trebler, H. A., U. S. Pat. 2,071,368 (February 23, 1937).
123. Whittier, E. O., *J. Dairy Sci.* **27**: 505 (1944).
124. Whittier, E. O., and Rogers, L. A., *Ind. Eng. Chem.* **23**: 532 (1931).
125. Whitnah, C. H., *J. Am. Chem. Soc.* **53**: 300 (1931).
126. Wilster, G. H., "Practical Butter Manufacture." 6th ed. Corvallis, Ore., Oregon State Coll. Coop. Assoc. (1948).
127. Wright, N. C., *J. Dairy Res.* **4**: 122 (1932).

Chapter VI

THE CHEMISTRY OF EGGS AND POULTRY PRODUCTS

R. M. Conrad [*]

University of Denver, Denver, Colorado

Chemical Composition of Normal Eggs

Because of its great economic importance as a food, as well as its fundamental importance in biological science, the egg of the domestic hen has been investigated from many points of view. As might be expected, its chemical composition has been the subject of several reviews.[5, 11, 16] A study of the data included in these reviews is likely to impress the reader with the great variability in what is usually considered a standard product. Even the percentage of the whole egg made up by its major parts—white, yolk, and shell—varies within wide limits as shown in Table 53.[11, 16] In compiling this table an attempt has been made to eliminate data from eggs that apparently were definitely abnormal, such as double-yolked eggs.

Table 53. Variations in White, Yolk and Shell of Eggs

	Maximum %	Minimum %	Representative Value %
White	62.7	46.7	58
Yolk	41.3	25.2	31
Shell	14.0	6.3	11

There is every reason to believe that the composition of each of these major parts of the egg is subject to less variation in composition than is the whole egg. The reason for some of these variations will be discussed later. As a basis for that discussion, data which may be considered representative of the composition of white, yolk, and shell have been selected and are presented in Tables 54 and 55.[5, 11, 16, 24]

It is difficult to include in tables such as these many of the interesting facts which have been learned about the composition of egg. For example, chemical analysis tells us only how much protein is present. Studies of the quality of this protein indicate that the mixture of protein present in the whole egg is one of the most efficient sources of dietary protein, having a biological value of 97 and true digestibility of 96.[27] Furthermore,

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[*] Dr. Conrad died shortly after he had completed the manuscript of this chapter. Several of his former colleagues in the Institute of Industrial Research of the University of Denver have assisted in preparing this material for publication: their help is gratefully acknowledged. Ed.

TABLE 54. CHEMICAL COMPOSITION OF EDIBLE PORTIONS OF EGGS

	White %			Yolk %		
Water			86.6			49.0
Organic Material:						
Proteins:						
Ovoglobulin	6.7				- - -	
Ovomucin	1.9				- - -	
Ovalbumin	69.7				- - -	
Conalbumin	9.0				- - -	
Ovomucoid	12.7				- - -	
Vitelline		- - -		78.4		
Livetin		- - -		21.6		
Total Protein	100.0%	-	11.6	100.0%	-	16.7
Lipids:						
Neutral fats		- - -		51.2		
Lecithin		- - -		34.2		
Cephalin		- - -		8.9		
Cholesterol		- - -		5.7		
Total Lipids			0.2	100.0%	-	31.6
Fat Acids of lipids:						
Myristic		- - -		0.4		
Palmitic		- - -		27.9		
Stearic		- - -		6.1		
Palmitoleic		- - -		2.0		
Oleic		- - -		48.5		
Linoleic		- - -		8.4		
Clupanodonic		- - -		6.7		
Total Fat Acids				100.0%		
Free carbohydrate as Glucose			0.4			0.21
Vitamins:		per 100 g.			per 100 g.	
Vitamin A		- - -			1100-4500 I.U.	
Vitamin D		- - -			50- 300 I.U.	
Thiamine		- - -			250- 480 γ	
Riboflavin		200-500 γ			600-1200 γ	
Pantothenic Acid		70-2500 γ			4000-6000 γ	
Nicotinic Acid		70-1000 γ			35-3000 γ	
Pyridoxin		- - -			2500 units	
Biotin		15 γ			50 γ	
Choline		- - -			1700 mg	
Luteol		- - -			7.3 mg	
Zeaxanthol		- - -			3.1 mg	
Other nitrogen-free organics			0.4			0.99
Inorganic Material:						
Calcium	0.014			0.131		
Chlorine	0.169			0.178		
Copper		- - -		0.000041		
Fluorine		- - -		0.00009		
Iron	0.0001			0.0087		
Magnesium	0.011			0.017		
Manganese		- - -		0.00105		
Phosphorus	0.015			0.607		
Potassium	0.152			0.115		
Sodium	0.162			0.049		
Sulfur	0.202			0.205		
Zinc		- - -		0.0005		
Bicarbonate	0.571					
Ash			0.8			1.5
			100.0%			100.0%

as might be expected, the yolk, and to a lesser degree the white, have been shown to contain enzyme systems.[16]

White. As can be seen in Table 54 the white of the egg is essentially a solution of proteins and inorganic salts in water. It will be noted that the inorganic salts include a large amount of bicarbonate but practically no phosphate. The fact that the inorganic buffer system is primarily bicarbonate gives the egg peculiar properties from the point of view of the processor who may wish to store it. In storage the bicarbonate loses carbon dioxide by diffusion through the shell with a resulting increase in pH. These changes will be discussed in more detail in a later section. Of the proteins present in the white apparently all are present in simple solution except for ovomucin. The ovomucin is present as the structural protein of the gelatinous part of the white and also in the white stringy chalazae which support the yolk in the center of the egg. Recent electrophoretic studies of the soluble proteins of egg white have shown that "ovalbumin" includes two fractions, and "ovoglobulin" can be separated into three distinct proteins.[23]

TABLE 55. COMPOSITION OF THE SHELL OF EGGS

	%
Calcium carbonate	93.7
Magnesium carbonate	1.39
Phosphate [P_2O_5]	0.76
Organic matter	4.15

It has long been recognized that egg white contains some material, known as lysozyme, capable of dissolving some bacteria. This has recently been isolated and identified as one of the fractions of ovoglobulin.[1] Another protein of the white has been found to combine with biotin in such a way as to render it nutritionally unavailable. It has recently been isolated and designated as "avidalbumin."[17] Since its nutritional effect was recognized long before its identification as a protein, it was formerly known as avidin.

In freshly laid eggs four layers of white have been described—a layer of thin white next to the shell, the thick white which is structurally a mucin gel, the inner thin white between the yolk and the thick white envelope, and finally, the chalaziferous layer, a very thin mucin film on the surface of the yolk. There is practically no difference in the composition of these four layers except for the presence of mucin in two of them. It has been demonstrated[9] that the inner thin white, the chalazae, and chalaziferous white result from the mechanical segregation of mucin from the original thick white gel.

Yolk. The yolk is made up very largely of an emulsion of very small fat droplets within a protein solution. It has been demonstrated that in the undisturbed yolk over half of the phospholipids are combined with protein rather than free. The two lipoproteins isolated make up 31 per cent of the solids of the yolk. It may be assumed that these lipoproteins exist to a large extent in the interfaces of the emulsion.[15, 33] Because of the high concentration of fat in the yolk the fat soluble vitamins and pigments of the egg are found here.

Shell. The shell of the egg is about 93 per cent calcium carbonate. Small amounts of other inorganic materials are present, but the only other important constituent is the protein. This protein includes the shell membrane made up of a fibrous protein usually considered a keratin, the shell matrix which appears to be made up of the soluble proteins of the white which have been denatured on the surface of the growing calcite crystals, and the cuticle, a surface layer of protein which is probably largely a form of mucin. Structurally the shell contains minute pores which are important in consideration of keeping quality because they provide access for microorganisms, and means of escape of carbon dioxide and water.

Factors Influencing Composition of Fresh Eggs

It should be recognized that the figures given in Table 54 represent only a representative composition of the egg. Several factors may cause comparatively large deviations from these values. The most important of these influences are breed, diet, and climate.

Breed. The most obvious difference in eggs laid by different breeds is in the color of the shell. Eggs laid by the heavy breeds, such as the Plymouth Rocks and Rhode Island Reds, have a brown shell color due to the presence of a porphyrin pigment in the outer layers of the shell.[16] In the Mediterranean breeds, this pigmentation is absent, and as a result the shell color is white.

A much more important difference in the composition of eggs laid by different breeds is in the relative size of the yolk. Czadek[12] reports a range from 30.2 per cent of the egg contents for Minorcas to 46.9 per cent for an Orpington. There is a strong indication that the percentage of yolk varies inversely with the size of the egg. However in eggs of very nearly the same size, Grossfeld[16] shows a spread from 29.4 per cent for Rhode Island Reds to 34.2 per cent for Orpingtons.

Little work has been published on the variations in the various proteins of the egg. However it has been observed that the amount of mucin present in the white varies from hen to hen.[10] It might be suspected from this that differences do exist between breeds and strains of poultry in the amount of the various proteins deposited in the white.

A marked breed difference has been found in the ability of the hen to deposit thiamine in the egg.[32] When maintained on the same diet, White Leghorn hens were found to deposit 279γ of thiamine in 100 g. of egg contents as compared with 167γ for Rhode Island Reds and 175γ for Barred Rocks.

Diet. It has been recognized for years that adequate supplies of calcium and vitamin D in the diet are necessary for normal shell formation.[8] The amount of shell deposited on the egg can be rather seriously reduced by a dietary insufficiency in either of these constituents. It is also well recognized that the amount of most of the vitamins deposited in the egg vary within wide limits, as shown in Table 54, and that this variation is largely influenced by the amount of the vitamin in the diet.[5]

Probably the most misleading of the data presented in Table 54 are the amounts of the various fatty acids present in the lipids of the yolk. Grossfeld [16] cites iodine numbers of the yolk fat which vary from 52.3 in eggs from hens fed a lipid-free ration to 120.9 when the hens were fed hemp seed. Cruickshank [11] points out that such very high iodine numbers occur only when fairly large amounts of unsaturated fats are present in the diet. Even so, it is obvious that no analysis of fatty acids can be truly representative of eggs in general.

The yellow pigments of the yolk have been shown to include luteol, zeathanthol, and cryptoxanthol with traces of carotene. Except for carotene, which is largely converted to vitamin A by the hen, these pigments vary within wide limits determined almost entirely by their abundance in the diet.[29] By means of special experimental diets, the color of the yolk can be made to vary from a creamy white to a reddish orange. Since very little of the vitamin A activity of the yolk is present in the form of carotene, its color is by no means an infallible index of its vitamin content. However, since a high color is usually a result of an abundance of fresh green feed in the diet, it frequently is associated with a high content of vitamin A as well as the other vitamins abundant in grass and other leafy feeds.

In addition to what may be considered normal constituents of the egg, there are a number of substances which, when included in the diet, find their way into the egg. In this class we find several fat soluble dyes, selenium, and gossypol. The latter, a constituent of cotton seed meal, causes an objectionable, olive discoloration of the yolk when the eggs containing it are held in cold storage.[36]

Climate. Comparatively little work has been done on the effect of climatic influences on the composition of the egg. What information is available indicates that they may be important factors in causing differences in composition and deserve much more study. It has been shown that high temperatures decrease the amount of shell as well as total size of the egg.[38,39]

During the recent war, when large amounts of frozen and dried eggs were purchased by government agencies on rigid specifications, it was frequently observed that early spring eggs from the northern sections of the country were abnormally low in total solids. Whole eggs as broken out in a commercial plant usually contain from 26.0 to 27.0 per cent of solids.

Under the conditions mentioned, the solids content sometimes dropped as low as 25.0 per cent. Such a small difference might have little significance if observed in only a few eggs. When observed in thousands of pounds of eggs produced in a wide area, it is rather convincing evidence of a climatic influence on composition. The only explanation which has been advanced is that cold weather causes a decrease in the fat content of the yolk. It has been observed [10] that the fat content of yolks of eggs laid by hens under normal conditions increased from 30.8 to 32.9 per cent from January to May, while in otherwise identical birds kept in a constant temperature room, no similar increase occurred.

STORAGE OF EGGS

Because of the natural reproductive habits of the hen, more eggs are always produced in the spring than during the rest of the year. In 1918 it was stated that 50 per cent of the eggs laid in this country were produced in March, April, May, and June.[13] The distribution throughout the year is no doubt more uniform now because of improvements in breeding and management, but the fundamental problem still exists of holding the spring surplus for fall and winter consumption.

Until about 1912, storage of eggs was entirely a matter of the preserving of the egg in its shell. Since that time, there has been a gradual increase in the storage of eggs in the broken-out, frozen form, and as dried egg products.[22, 34]

Shell Eggs. The changes which take place in shell eggs during storage, and the means of retarding these changes have been discussed in excellent reviews.[18, 34] In general, these changes may be classed as physical and chemical or as microbiological. As might be expected, both types can be retarded but not entirely eliminated by storage at low temperatures. Actual freezing of shell eggs is likely to break the shell, so that in commercial installations, eggs are stored just above their freezing point, at a temperature of 30–32° F.

The physical and chemical changes are closely related and cannot be entirely separated. The first of these is the loss of water by evaporation through the pores of the shell. This can be observed, when the egg is candled, by an enlargement of the air cell. In practice this is an important measure of egg quality, since it is an easily observed change. However, there is little if any reason to believe that loss of water alone and within reasonable limits causes any real loss in quality. In order to control the loss of moisture, egg storage rooms are usually kept at relative humidities of about 90 per cent, and the shells are frequently sealed with a thin film of mineral oil.

A far more important change closely related to the loss of moisture is the loss of carbon dioxide through the pores of the shell. It has already been pointed out that the buffer of the white is primarily a bicarbonate solution. In the freshly laid egg, the pH of the white is 7.6 and of the yolk 6.0.[34] The white has a CO_2 tension approximately equal to an atmosphere containing 10 per cent CO_2. As a result, the white rapidly loses CO_2 until within a few days the pH has reached a value of approximately 9.0. The increase in pH causes at least two undesirable changes in the structure of the egg contents. The mucin of the thick white loses much of its gelatinous quality, so that the thick white becomes flabby, and the egg spreads out when fried or poached. In addition, the vitellin membrane which surrounds the yolk is weakened and becomes more permeable to water. Water diffuses from the white into the yolk, which because of its enlargement and the weakening of the membrane is likely to break when the egg is opened.[18]

These changes have been controlled by storage in an atmosphere containing CO_2 and by sealing the shell with oil.[18, 34] Both methods are difficult to apply until the egg has reached commercial channels, by which time considerable damage has already occurred. It has been found that high concentrations of CO_2 in the storage atmosphere tend to cause the thick white to shrink and to appear milky, so that a concentration of 1 per cent has been selected as most desirable.[34]

The most promising method of preserving the original quality of shell eggs appears to be the oiling of the eggs on the farm the day after laying.[14] Such treatment greatly retards the changes that normally take place before the egg reaches commercial storage, as well as those taking place in storage.

Because of the high humidity usually maintained in egg storage rooms, mold growth is common. As a matter of fact, "whiskers" on eggs after several months of storage are sometimes used as an indicator of favorable humidity conditions. Occasionally molds penetrate the shell and grow within the egg. It has been proposed to control mold growth on eggs in storage by impregnating the flat and fillers in which the eggs are packed with sodium pentachloro phenate.[26]

A far more serious microbiological problem is the growth of bacteria within the egg. It has repeatedly been demonstrated that the contents of fresh, clean eggs are usually sterile, and that bacterial spoilage of eggs in storage results from penetration of the shell by the organisms after laying. The most important cause of such invasion is undoubtedly the washing of dirty eggs, but it is also likely that the "sweating" of eggs when brought out of a cold room is another potent cause of invasion. Cleanliness in the production of eggs is by far the best means of preventing bacterial spoilage. It has been suggested that invasion may be reduced by sealing the shell with oil containing a bactericide,[25] or that bacteria already in the egg may be killed by carefully controlled heat treatment.[2]

Frozen Egg Products. Since its beginning, there has been a steady increase in the practice of supplying eggs to industrial users in the form of broken-out frozen egg products. The system has two outstanding advantages: (1) deterioration, which is very serious in cold storage shell eggs, is no problem in frozen eggs stored at a temperature of 0° F. or below, and (2) it is a great convenience to large users to receive eggs already broken out and, when desired, separated into whites and yolks.

LeClere and Bailey[22] have reviewed the uses of frozen egg products in the prewar period. They report that about half the total volume of frozen egg products was represented by whole egg, nearly all of which went into the bakery trade. Whites and yolk products each represent approximately an additional quarter. The whites are also used largely in bakeries, with another important use in candy manufacture. Yolks are packed in several ways: (1) as plain frozen yolks, which are used in bakery goods, mayonnaise and salad dressing, and in noodles, (2) as yolks with salt added, used entirely in mayonnaise and salad dressing, and (3) with sugar or glycerine added, in which form they are used primarily in bakery goods.

It has been stated[34] that egg white is not altered by freezing. However, it is recognized that a very profound change takes place when whole egg or yolk is frozen and thawed. This change has long been associated with the lecitho-protein,[34] and recently it has been pointed out that one of these, lipovitellenin, becomes much less soluble when frozen and thawed.[15] The change is apparent by a great increase in viscosity, and yolk may even become tough and rubbery, making it difficult to use. The addition of salt, sugar, or glycerine are common measures taken to prevent this change. It has been suggested that their effect is simply to lower the freezing point of the product, but it seems more likely in the light of recent work[7, 15] that the effect is a more complicated one.

TABLE 56. MINIMUM SOLID CONTENT OF FROZEN EGG PRODUCTS

	Egg Solids %	Other %
Whole egg	26.0	--
White	11.5	--
Yolk	43.0	--
Sugared yolk	38.7	10 sugar
Salted yolk	38.7	10 salt

While the composition of frozen egg products varies somewhat as might be expected from the previous discussion of variation in composition of fresh eggs, commonly accepted minimum solids content are presented in Table 56 for reference. It will be observed that the solids-content given for yolk products is less than might be expected from Table 54. The reason for this discrepancy is that under commercial conditions it is not practical to separate completely the yolk from the white, and commercial yolk may contain up to 12 per cent white.[22]

Dried Egg Products. Although dried egg products are nearly as old as frozen egg products, until the recent war comparatively small amounts were produced.[22] Nearly all of this was in the form of dried yolk and white. The yolks were used in such products as doughnuts, noodles, and pancake flour where the foaming characteristic of the yolk is not of great importance. The whites were used largely in candy manufacture. With the increasing interest in premixed cake flours, and as a result of the great improvement in quality of dried egg products made possible by recent research it is probable that there will be a marked increase in the egg drying industry.

The reasons for the slow development of the drying industry can be found in the failure of its products to compare in quality and performance with frozen egg products. In dried whole egg and yolk, three types of damage have been characterized: (1) a gradual loss of solubility during storage, (2) inability to produce a foam comparable to fresh or frozen egg, and (3) the development of a characteristic off-flavor during storage.

The loss of solubility has been associated with a condensation between reducing sugar and free-amino groups of the proteins, and can be controlled by drying to low moisture levels, slight acidification, and storage under refrigeration.[3]

The second type of damage has been shown to occur during the drying operation, rather than during storage, and to result from a weakening of the association between lipids and proteins and an increase of free phospholipids.[7] The loss of foaming quality can be completely prevented by the addition of sugar to the liquid egg before drying. The resulting dry product performs as well as fresh or frozen eggs in such bakery goods as sponge cakes, which depend upon the foaming characteristic of the egg used. Since this product is intended for bakery use, the sugar content is not objectionable. However, the addition of sugar in some manner increases the susceptibility of the product to a type of oxidative deterioration which results in a fishy flavor. For this reason, dried egg products containing sugar must be packed in vacuum or inert gas if they are to be stored for any appreciable length of time.

The flavor deterioration of dried egg products was of greatest concern in connection with the huge amounts of dried whole egg supplied to our armed forces and allies during the war. It has been found to be associated with the same type of amine-aldehyde condensation which causes the loss of solubility. However, since it is also related to oxidative changes, it is probable that there is some condensation with aldehyde groups formed by fat oxidation, and since the characteristic flavor develops only in products containing egg fat, the amino groups of the phospholipids are also probably involved. The mechanisms of this reaction as well as means of controlling it have been studied by Boggs and Fevold,[6] who have found that the rate of development of off-flavor can be reduced by each of three different steps: (1) drying to moisture levels of 2 per cent or less, (2) storage under inert gas, and (3) acidification of the liquid egg to a pH of 5.5 before drying. By a combination of these three steps, dried whole egg has been produced on a commercial scale which maintained a satisfactory flavor for six months when stored at a temperature of 100° F. This represents a flavor stability which should be sufficient for any practical purposes.

TABLE 57. CHEMICAL COMPOSITION OF EDIBLE PORTIONS OF CHICKENS AND TURKEYS

Kind of Fowl	Protein %	Fat %	Ash %	Water %
		Breast Muscle		
Chickens, male	23.5	1.12	1.11	74.6
Turkeys, male	24.6	1.03	1.16	73.4
Turkeys, female	24.8	1.12	1.20	73.1
		Leg Muscle		
Chickens, male	20.1	4.39	1.05	74.5
Turkeys, male	20.7	4.00	1.06	73.7
Turkeys, female	20.7	4.77	1.05	73.2
		Remaining Edible Portion		
Chickens, male	17.3	24.1	0.79	57.6
Turkeys, male	16.3	33.6	0.70	49.6
Turkeys, female	13.9	41.4	0.65	43.6
		Total Edible Portion		
Chickens, male	19.9	10.9	0.97	68.3
Chickens, female	19.3	11.9	1.09	65.8
Capons	18.7	11.9	1.03	66.2
Turkeys, male	20.6	12.7	1.00	65.8
Turkeys, female	19.4	17.9	0.95	61.8

Dried egg white represents a much less complicated system than whole egg or yolk. Even in this case, however, a condensation between reducing sugar and protein occurs, which reduces the solubility of the protein and hence its ability to foam. Since dried white is used primarily for its foaming or whipping quality, this is a fatal defect. This type of deterioration has been controlled by fermentation of the white to remove the sugar before drying.[35] Fermentation has been a common and almost universal practice for many years. When the sugar has been properly removed by this method, dried egg white is an extremely stable product. The common method of fermenting white is to allow the white to stand at a temperature of about 80° F. until the bacteria naturally present have converted the sugar to lactic acid and carbon dioxide. The lactic acid formed causes the pH to fall from 9.0, the normal value in commercial white, to below 6.0. At this pH the ovomucin is precipitated and rises to the top with the foam and is removed before drying.

POULTRY MEAT

Poultry meat differs only in minor degree from other meats. Harshaw [20] has summarized analyses of chicken and turkey meats (Table 57). Obviously the amount of fat will depend on the previous diet and age of the individual bird, as is true of other animals. Analyses of poultry muscle proteins for ten amino acids have indicated no appreciable differences from beef, pork, and mutton proteins.[4] The fat of chickens and turkeys is in general more saturated than that of fish and less saturated than that of beef and pork. The analytical characteristics of commercial samples of poultry fat are given in Table 58.[28] Lea [21] reports that poultry tissues contain a lipase which causes more rapid breakdown of the fat than occurs in mammalian tissues. It is commonly believed that turkey fat becomes rancid more easily than chicken fat. However, Table 58 reveals no reason for this, and it has been reported [28] that when samples of fat are taken from freshly killed birds, both turkey and chicken fat are equally stable. The difference observed in practice may be due to the fact (undemonstrated) that turkey tissues contain more of the lipase mentioned by Lea, or it may be that because of their larger size, turkey carcasses cool more slowly than chickens, allowing more time for autolysis. It has been demonstrated that in chickens, holding the carcass at temperatures above freezing greatly increases the susceptibility of the fat to oxidation.[37]

TABLE 58. COMPOSITION OF CHICKEN AND TURKEY FATS [28]

	Chicken Fat	Turkey Fat
Free fatty acids (as % oleic)	0.75	2.26
Saponification no.	182.9	184.5
Iodine no.	79.1	78.4
SCN no.	60.5	59.6
Ref. index 40° C.	1.4612	1.4610
Fatty acids (%)		
Saturated	32.8	33.7
Unsaturated	67.2	66.3
Linoleic	20.6	20.8
Oleic	46.6	45.5

In a study of the B-complex vitamins of various chicken muscles, it was found that dark meat contained two to three times as much thiamine.

riboflavin, and pantothenic acid as the light meat, but the situation was reversed with respect to niacin.[30] The values reported are summarized in Table 59.

TABLE 59. VITAMIN CONTENT OF CHICKEN MEATS

	Micrograms Vitamin per Gram of Tissue
Thiamine	0.5 - 1.4
Riboflavin	0.5 - 4.9
Niacin	45.0 - 135.5
Pantothenic Acid	1.1 - 10.6

Another interesting difference between the light and dark meat is that the former has been observed to pass through rigor and become tender several times as rapidly as the dark meat.[19]

Poultry is usually stored in the frozen state with the viscera intact, although the practice of evisceration has increased greatly in the past few years. The fact that the skin protects the bird tends to minimize "drip" on thawing, which is frequently serious in other frozen meats. Otherwise, the behavior of poultry meat in storage is similar to other meats, modified, of course, by the greater unsaturation of the fat, the presence of the lipase mentioned previously, and the diffusion of visceral flavors into the meat when stored uneviscerated.

BIBLIOGRAPHY

1. Alderton, G., Ward, W. H., and Fevold, H. L., *J. Biol. Chem.* **157**: 43 (1945).
2. Barott, H. G., and McNally, E. H., *U. S. Egg Poultry Mag.* **49**: 320 (1943).
3. Bate-Smith, E. C., and Hawthorne, J. R., *J. Soc. Chem. Ind.* **64**: 297 (1945).
4. Beach, Eliot F., Munks, Bertha, and Robinson, Abner, *J. Biol. Chem.* **148**: 431 (1943).
5. Bird, H. R., *U. S. Egg Poultry Mag.* **49**: 402, 419 (1943).
6. Boggs, M. M., and Fevold, H. L., *Ind. Eng. Chem.* **38**: 1075 (1946).
7. Brooks, J., and Hawthorne, J. R., *J. Soc. Chem. Ind.* **63**: 310 (1944).
8. Buckner, G. Davis, Martin, J. Holmes, and Insko, W. M., Jr., *Am. J. Physiol.* **94**: 692 (1930).
9. Conrad, Ralph M., and Phillips, R. E., *Poultry Sci.* **17**: 143 (1938).
10. Conrad, Ralph M., and Scott, H. M., *Proc. Seventh World's Poultry Congress* 528 (1938).
11. Cruickshank, E. M., *Chem. Ind.* **59**: 415 (1940).
12. Czadek, O. v., *Z. landw. Versuchswesen Osterreich.* **19**: 440 (1916).
13. Dvoracheck, H. E., and Stout, S. R., *Arkansas Expt. Sta. Bull.* **152**: 1 (1918).
14. Evans, Robert J., and Carver, J. S., *U. S. Egg Poultry Mag.* **48**: 546 (1942).
15. Fevold, H. L., and Lausten, Adele, *Arch. Biochem.* **11**: 1 (1946).
16. Grossfeld, J., "Handbuch der Eierkunde." Berlin, Julius Springer (1938).
17. Gyorgy, Paul, Rose, Catherine S., Eakin, Robert E., Snell, Esmond E., and Williams, Rodger J., *Science* **93**: 477 (1941).
18. Haines, R. B., *Chem. Ind.* **59**: 391 (1940).
19. Hansen, Helen L., Stewart, George F., and Lowe, Belle, *Food Research* **7**: 148 (1942).

20. Harshaw, H. M., U. S. Dept. Agr., Bur. Animal Ind., Animal Nutr. Div. A.N.D. No. 7 (1942).
21. Lea, C. H., "Rancidity in Edible Fats." New York, Chemical Publishing Co. (1939).
22. LeClerc, J. A., and Bailey, L. H., *Cereal Chem.* **17**: 279 (1940).
23. Longsworth, Lewis G., Cannan, R. Keith, and MacInnes, D. A., *J. Am. Chem. Soc.* **62**: 2580 (1940).
24. McNally, E. H., and Denton, C. A., Mimeo. Table Distributed by Bur. Animal Ind., U. S. Dept. Agr., Beltsville, Md.
25. Mallman, W. L., and Davidson, J. A., *U. S. Egg Poultry Mag.* **50**: 169, 189 (1944).
26. Mallman, W. L., and Michael, Catherine E., *Michigan Agr. Expt. Sta. Tech. Bull.* **174** (1940).
27. Murlin, John R., Edwards, Leslie E., and Hawley, Estelle E., *J. Biol. Chem.* **156**: 785 (1944).
28. Nutter, Mary K., Lockhart, Ernest E., and Harris, Robert S., *Oil and Soap* **20**: 231 (1943).
29. Peterson, W. J., Hughes, J. S., and Payne, L. F., *Kansas Agr. Expt. Sta. Tech. Bull.* **46** (1939).
30. Rice, E. E., Strandine, E. J., Squires, E. M., and Lyddon, B., *Arch. Biochem.* **10**: 251 (1946).
31. Rose, M. S., and Vahlteich, E. M., *J. Am. Dietet. Assoc.* **14**: 593 (1938).
32. Scrimshaw, Nevin S., Hutt, F. B., Scrimshaw, Mary W., and Sullivan, C. R., *J. Nutrition* **30**: 375 (1945).
33. Sell, H. M., Olsen, A. G., and Kremers, R. E., *Ind. Eng. Chem.* **27**: 1222 (1935).
34. Sharp, Paul F., *Food Research* **2**: 477 (1937).
35. Stewart, G. F., and Kline, R. W., *Proc. Inst. Food Technologists* **1941**: 48.
36. Swenson, A. D., Fieger, E. A., and Upp, C. W., *Poultry Sci.* **21**: 374 (1942).
37. Wagoner, C. E., Vail, Gladys E., and Conrad, R. M., *Poultry Sci.* **26**: 170 (1947).
38. Warren, D. C., *J. Agr. Research* **59**: 141 (1939).
39. Warren, D. C., and Schnepel, Richard L., *Poultry Sci.* **19**: 67 (1940).
40. Warren, D. C., and Conrad, R. M., Unpublished data.

PART II

FERTILIZERS AND SOIL AMENDMENTS

Chapter VII

NITROGENOUS FERTILIZERS

S. F. Thornton

F. S. Royster Guano Co., Norfolk, Va.

In its free state, nitrogen is a colorless, odorless, inert gas that makes up about 80 per cent of the air around us. In the air over each acre of land there is a nitrogen supply of over 35,000 tons.

The supply of nitrogen is plentiful but this abundance occurs in a form that is of no value to most crops. Plants, except legumes, cannot use pure nitrogen nor can nitrogen be put into fertilizers in this form. It must be combined with other elements before it is of value as a plant nutrient or a fertilizer material.

Effect of Nitrogen on Growth and Development

In plant and animal nutrition, nitrogen very appropriately has been called the "growth element." It is a component of chlorophyll, of protein, and of many other compounds essential to plant and animal life.

An adequate supply of nitrogen is necessary for growth and reproduction in both plants and animals. In combination with carbon, hydrogen, oxygen and other elements it forms a vital component of every living cell and an essential part of all plant and animal tissue. Without nitrogen life would be impossible.

Growth and reproduction in plants are exceedingly complex processes. It follows, therefore, that the effects of nitrogen nutrition on plant life are varied and complicated. Among the more visible and more economically important of these effects are the following:

1. It increases general plant vigor.
2. It gives dark green color to leaves and other above-ground parts.
3. It promotes increased leaf and stem growth.
4. It increases yield of fruits and grains.
5. It adds crispness and improved quality to leaf crops.
6. It encourages rapid and vigorous early growth.
7. It increases the protein content of food and feed crops.
8. It hastens maturity when used in moderate amounts.
9. It may delay maturity when used in excessive amounts.

In contrast to plants abundantly supplied with nitrogen, those growing under conditions of nitrogen deficiency usually are small in size, stunted in growth and lacking in vigor. Typical symptoms of nitrogen deficiency are:

1. Loss of normal dark green color (Figure 2).
2. Pale, yellowish leaves (Figure 3).
3. Stalks that show an uncommon amount of pink or light red color.
4. Lower leaves that turn yellow or orange, often fire badly and sometimes shed prematurely.
5. Slender stalks and branches.
6. Slow growth and development.
7. Low yields.

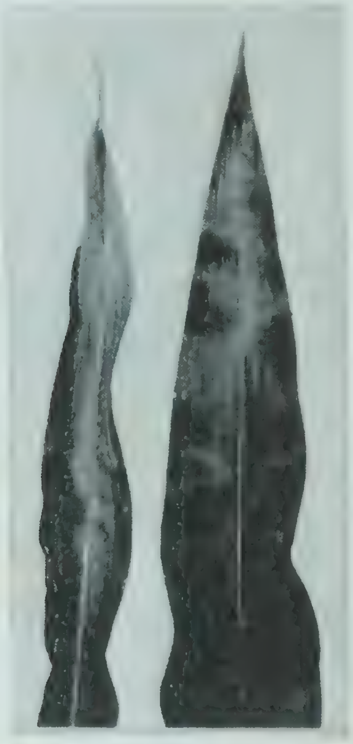

FIG. 2. Nitrogen deficiency symptoms on corn leaves. (*Right*) Normal Leaf. (*Left*) Leaf from nitrogen-deficient plant—note firing at tip and along midrib.

SOIL NITROGEN SUPPLIES

Total nitrogen supplies in most soils are small and in many are less than 1000 pounds per acre of surface soil. These total soil supplies are stored almost entirely in the organic matter or humus and represent accumulations resulting from ages of plant and animal growth and decay. Common soil-forming minerals contain no nitrogen and so contribute nothing to the soil's nitrogen supply.

In the soil organic matter the nitrogen is tied up in complex chemical compounds that cannot be utilized by plants. Processes of decay must first break down these complex substances and convert the nitrogen into simpler forms that are more soluble and more readily available.

Plants, other than legumes, are dependent on the simpler, more soluble nitrogen compounds in the soil to supply their nitrogen needs. It is for this reason that even with soils well supplied with total nitrogen there often are periods when conditions are unfavorable for microbiological activity and the processes that result in the formation of soluble nitrogen compounds are slowed down to such an extent that supplies of available nitrogen become inadequate. This same temporary condition may come about as a result of heavy rains that dissolve soluble nitrogen compounds and take them down below the zone in which plant roots are active.

Chemical examination of arable soils shows the greater part of their soluble nitrogen content to be present in the nitrate form. Ammonium compounds and nitrites, the other most likely possibilities, seldom are found in any large quantities except under quite abnormal conditions. Because of this, it is not surprising to find that most of the nitrogen used by plants is taken up in the nitrate form.

These facts have led to the somewhat general conclusion that nitrogen must be in the nitrate form to be effectively utilized by growing crops. This belief is by no means true for there is abundant experimental evidence to show that ammonia and even some of the simpler organic nitrogen compounds can be directly and effectively taken up and utilized.[7, 14, 25, 26] Small amounts of nitrite nitrogen, likewise, can be utilized but large quantities appear to be definitely harmful.

The predominance of nitrate as the form of nitrogen used by plants is due almost entirely to soil conditions that favor its formation. As the insoluble and complex nitrogenous organic materials are broken down in the soil they are converted first into simpler organic compounds, then to ammonia, to nitrites, and finally to nitrates.

Nitrates are the final oxidation products of soil nitrogen and microbiological conditions in most cultivated soils favor their rapid formation. Nitrates thus accumulate in the soil until lost by leaching or used by growing plants. The simpler organic compounds, ammonia, and nitrites are only transition products in the conversion processes. They are constantly being formed in the soil but rapidly disappear as the conversion process goes toward completion and so seldom accumulate in large quantities.

THE NITROGEN DEFICIENCY PROBLEM

Recognition of the effect of nitrogen on crop production and of its importance in plant nutrition dates back to earliest time. Along with this recognition has gone an appreciation of the advantages of conserving and increasing available nitrogen supplies in the soil.

The work at Rothamsted, England, for example, illustrates and emphasizes this early interest in the nitrogen problem. This same interest in and attention to nitrogen can be traced down through the years in the writings of agricultural scientists and in the experiences of practical farmers in both Europe and America.

Years of study have brought much information about these problems but no final solutions. Due to low supply in most soils and to large losses through erosion, leaching and crop removal, nitrogen deficiency has become one of the most important agricultural problems all over the world.

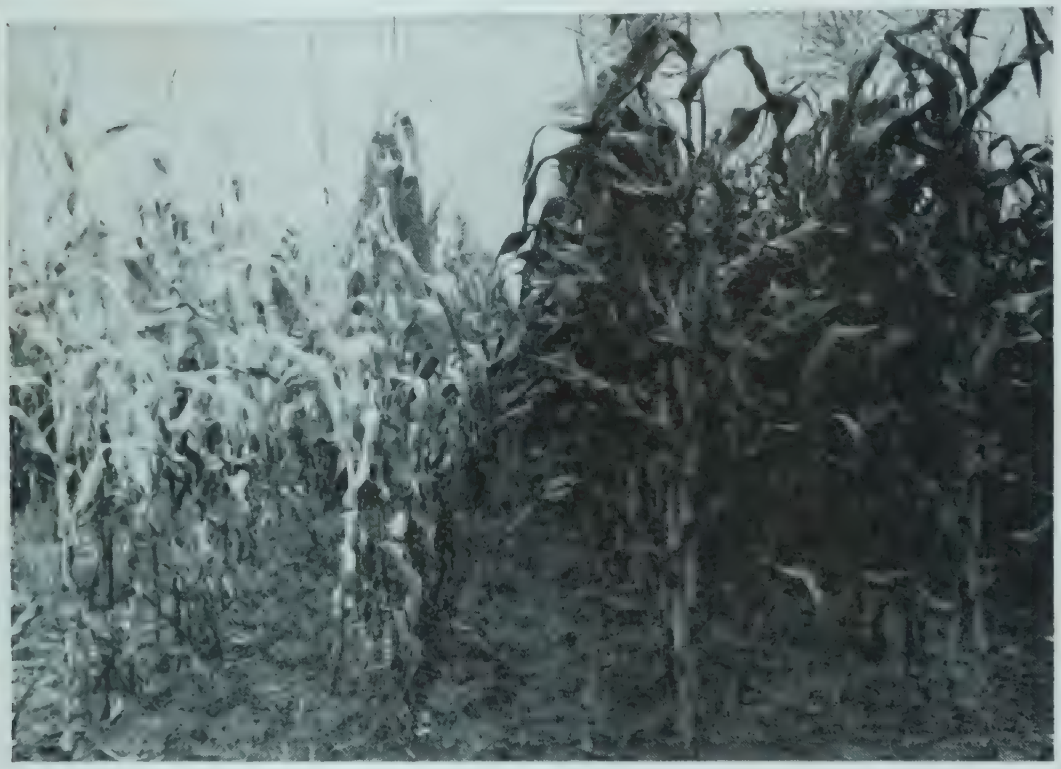

FIG. 3. Wherever crops are harvested, nitrogen deficiency is a problem that demands attention. (*Left*) No nitrogen—yield 24.4 bushels corn per acre. (*Right*) 180 pounds nitrogen—yield 110.3 bushels corn per acre. (Courtesy North Carolina Agricultural Expt. Station.)

This problem of nitrogen shortage in the soil is concisely stated by Parker,[16] who says that nitrogen is one of the most commonly deficient plant nutrient elements in the arable soils of the world and that, wherever crops are harvested, there is the problem of providing an adequate nitrogen supply. This is true, says Parker, whether we are thinking in terms of the alluvial soils of the Nile, the Ganges, and the Mississippi; the irrigated soils of Asia and western United States; or the soils of the tropics, the coastal plains and the prairies.

Parker further states that we may ignore the problem as is done in many places and take the consequences in declining yields and depleted soils. He recommends, however, that we adopt soil management practices needed to provide the nitrogen required at the right time and in the amounts needed for efficient crop production.

The major practices, listed as desirable and necessary parts of Parker's soil management program mentioned above are:

1. The growth of legume crops to build up nitrogen and organic matter reserves.
2. The use of close-growing nonlegumes, with or without supplementary nitrogen.
3. The conservation and use on the land of crop residues and farm manures.
4. The direct use of nitrogenous fertilizers to bring in extra supplies of this plant nutrient element from outside sources.

NEED FOR NITROGENOUS FERTILIZERS

The nitrogen problem is old, but the use of nitrogenous fertilizers, as we now know them, is a relatively modern custom. Only within the past century has the use of such fertilizers become an important practice. Prior to that time the farmer depended on the forces of nature and the use of animal manures, legume crops, and plant and animal residues.

The use of commercial nitrogenous fertilizer was looked upon as an unnecessary practice. It was believed that the greater part of the nitrogen needed to make up for losses brought about by leaching and by crop removal would be obtained from the vast storehouse of the air by the action of nitrogen-fixing bacteria growing in the nodules on the roots of legumes or living and working in the soil itself. It was recommended that these gains be supplemented by the conservation and return to the soil of animal manures and plant and animal residues.

This plan seemed largely justified as long as farming was kept on an extensive basis, as long as the available supply of land and labor made high yields per acre unnecessary, and as long as vast areas of new and highly productive land could be had almost for the asking. Under such conditions the prevailing scarcity and high cost of nitrogenous fertilizer and low returns from the crops produced made the use of large quantities of commercial nitrogen an unprofitable venture.

Such conditions no longer prevail. Land and labor are scarce and high in price. The big storehouse of nitrogen found locked up in the organic matter of many of our virgin soils has been used up at an alarming rate and now is seriously depleted. Products of the farm are short in supply and high in price. Fertilizer nitrogen is greatly increased in supply and low in price in comparison to the value of the yield increases it brings.

Intensive cultivation that results in high yields per acre now is the recommended and accepted practice. At the same time a smaller part of the total production of the land is used on the farm and a larger part taken off in harvested crops and each bushel of grain, each ton of hay, each pound of meat and each gallon of milk sold off the farm carries with it nitrogen that is lost to the soil. Under such conditions, experience has shown that there is likely to be a gradual depletion of nitrogen supplies in the soil and eventually a shortage that brings reduced crop yields. At this stage, under most systems of farming, the use of nitrogenous fertilizers to bring in extra supplies from outside sources becomes a necessary requirement for continued high production.

Table 60. Nitrogen Removed by Farm Crops

Crop	Part Harvested	Acre Yield	Nitrogen Removed lb. per Acre
Alfalfa	Hay	4 tons	190
Apples	Fruit	300 bus.	17
Barley	Grain	30 bus.	27
Barley	Straw	0.8 ton	9
Bluegrass	Hay	1 ton	27
Cabbage	Heads	10 tons	60
Clover	Hay	2 tons	82
Corn	Ears	60 bus.	57
Corn	Stover	2 tons	36
Corn	Silage	12 tons	82
Cotton	Lint and Seed	1,500 lbs.	40
Cotton	Stalks	2,800 lbs.	35
Cow peas	Grain	15 bus.	34
Cow peas	Hay	2 tons	100
Mangels	Roots	40 tons	175
Oats	Grain	50 bus.	32
Oats	Straw	1 ton	12
Onions	Bulbs	600 bus.	92
Peaches	Fruit	500 bus.	30
Peanuts	Nuts	2,000 lbs.	70
Peanuts	Vines	2 tons	85
Potatoes [Irish]	Tubers	300 bus.	63
Potatoes [Sweet]	Tubers	300 bus.	40
Rye	Grain	30 bus.	32
Rye	Straw	1.5 tons	14
Soybeans	Grain	20 bus.	70
Soybeans	Hay	2 tons	102
Spinach	Tops	500 bus.	44
Sugar beets	Roots	15 tons	76
Timothy	Hay	1.5 tons	30
Tobacco	Leaves	1,000 lbs.	44
Tobacco	Stalks	450 lbs.	15
Tomatoes	Fruit	8 tons	32
Turnips	Roots	400 bus.	51

Nitrogen Losses from Soils

Nitrogen losses from cultivated soils are large and never ceasing. The principal causes of such losses are leaching, erosion, and crop removal. Denitrification and decay processes account for smaller and much less important losses.

Leaching and erosion losses are known to be large but are difficult to evaluate in the form of definite figures. Losses due to removal of crops and animals grown on the farm, on the other hand, can be reduced more easily to definite values.

Leaching losses are concerned chiefly with nitrogen in the nitrate form. Nitrates move readily in the soil moisture and, in periods of heavy rainfall, may be temporarily taken down below the zone where plant roots are active or even carried away and permanently lost to the soil. The principal factors determining the amount of nitrogen lost from a soil by leaching are the physical properties of the soil; the quantities of available nitrogen, especially nitrates, in the soil; the kind of crops grown; the extent to which growing crops are kept on the soil; the amount and distribution of the rainfall; and temperature and other weather conditions.

The greater part of the soil's nitrogen supply is contained in the topsoil. When this topsoil is lost by erosion the reserve nitrogen supply is seriously depleted. All forms of nitrogen present in the soil share equally in such losses.

Crops require large quantities of nitrogen in their growth and development. When these crops are harvested and sold off the farm this nitrogen goes along with them and so is lost to the farm.

The quantity of nitrogen removed from the soil in harvested crops is highly variable from field to field and from season to season. The more important factors determining this are the type of crop grown, the acre yield, the maturity of the crop at harvest time, and the supply of available nitrogen accessible to the crop.

TABLE 61. ANNUAL NITROGEN LOSSES FROM THE SOILS OF THE UNITED STATES

Methods of Loss	Nitrogen Tons
Harvested crops	4,611,210
Grazing	8,293,200
Leaching	5,000,000
Erosion	4,994,636
Total	22,899,046

With legume crops special consideration must be given to the fact that a considerable part of their nitrogen content comes from the air rather than from the soil. Thus the nitrogen left in the soil by roots and other residues of legume crops often more than makes up for the quantities taken from the soil in the harvested portions.

The nitrogen content of a number of the more important harvested crops is shown in Table 60. These data emphasize the heavy demand made on the soil's nitrogen reserve by growing crops.

An estimate of the total nitrogen losses from the soils of the United States for 1930 has been reported by Lipman.[9] Data from this report are given in Table 61.

NITROGEN ADDITIONS TO SOILS

The indicated magnitude of nitrogen losses from the soil emphasizes the necessity of doing everything possible to conserve reserves now in the soil, to replace unavoidable losses, and to build up supplies where they already are low. Only in this way is it possible to arrive at anything like a satisfactory balance between losses and gains.

Fortunately, large quantities of nitrogen are added to the soil each year to partly counterbalance losses. Thus, along with the estimated 22,899,046 tons of nitrogen lost each year, Lipman[9] estimates nitrogen additions to the soil from all sources at 16,253,862 tons, leaving a net annual loss of 6,645,184 tons.

It is this continuing net loss of nitrogen from our soils that has made the use of nitrogenous fertilizer a necessary part of modern agriculture. Bringing in of extra supplies of nitrogen from outside sources makes it possible for the farmer to cultivate his land intensively and, year after year, to grow and harvest bumper crops.

This, however, does not mean that the use of nitrogenous fertilizer offers any complete solution to the nitrogen problem in agriculture. Commercial nitrogen, in the form of fertilizer, can never be more than a supplement to the much greater quantities of this plant nutrient element derived from the organic reserves in the soil, from farm manures, from crop residues, from biological fixation in the soil and on the roots of legumes and from the relatively large quantities of fixed nitrogen returned to the soil from the air in rain water.

The place of commercial nitrogen in this picture is made clear by a comparison of the quantities of nitrogen added to the soil annually by legume crops, by farm manures, and by nitrogenous fertilizers. In this connection, Parker[16] states that legumes supply far more nitrogen to the farm lands of the country as a whole than do farm manures and fertilizers combined. Farm manures, in turn, supply nitrogen far in excess of that contained in even the record quantities of fertilizer now being used.

Another indication of the relative importance of legume crops, farm manures and nitrogenous fertilizers as sources of nitrogen is given by the estimates of Lipman.[9] These estimates cover the year 1930 and show nitrogen addition to the soil in the form of legumes, manures, and fertilizers of 5,464,566 tons, 2,570,237 tons, and 304,864 tons, respectively.

FARM MANURE

Farm manure is not ordinarily classed as a commercial fertilizer and so, strictly speaking, is somewhat out of place in a discussion of nitrogenous fertilizers. However, the fact that it supplies such a very large quantity of nitrogen coupled with its almost universal use on the farms of the country make appropriate here a brief discussion of the composition, conservation, and value of farm manure.

An excellent discussion of this nature is given by Salter and Schollenberger [23] who in 1938 stated that the one billion tons of manure produced annually by the livestock on American farms is capable of producing crop increases worth $3,000,000,000. This gives a potential value to this farm by-product of three times that of the wheat crop or the equivalent of $440 for each of the country's 6,800,000 farm operators. The plant nutrients in this farm manure, if purchased in the commercial market in 1938, would have cost more than six times as much as was expended for commercial fertilizer in 1936.

Unfortunately, according to Salter and Schollenberger,[23] only a small fraction of the great potential value of manure is actually realized. This, they state, is due chiefly to the facts that about one-half of the total manure produced is dropped on pastures and uncultivated ground and that from the part handled as farm manure there are great losses because of failure to save the liquid portion, because of loss of nitrogen through improper fermentation and drying and because of leaching losses from storage piles exposed to rainfall. Other important factors in reducing the potential value of manure are probable losses through volatilization of ammonia when fermented manure is spread on the field and allowed to dry before it is incorporated in the soil and inefficient use because of failure to apply it at the season, in the manner, at the rate, or to the crop that gives the greatest return in increased production. On the basis of these facts, it is estimated that not more than a quarter to a third of the full potential value of farm manure is actually realized.

Farm manure is essentially a mixture of animal excrement, both liquid and solid, and bedding. It has a threefold value due to the three important materials it supplies to the soil—plant nutrients, organic matter, and growth promoting substances.

A ton of fresh manure contains, as an average, approximately 10 pounds of nitrogen, 5 pounds of phosphoric acid (P_2O_5), and 10 pounds of potash (K_2O), as well as important quantities of many secondary and minor plant nutrient elements needed by crops. In terms of a fertilizer grade manure, therefore, would be 0.50-0.25-0.50. On the basis of its nitrogen, phosphoric acid, and potash content alone, this makes 2000 pounds of manure the equivalent of 100 pounds of 10-5-10 fertilizer.

USE OF COMMERCIAL NITROGENOUS FERTILIZERS

During the early days of the existence of the fertilizer industry, the production of fertilizer was largely a scavenger business. Waste materials were gathered from all available sources and compounded into mixtures suitable for use on the farm.

Nitrogen came largely from plant and animal wastes and from guano and nitrate of soda imported from South America. Inorganic or mineral nitrogen was of relatively little importance in this picture until around the beginning of the twentieth century.

Since 1900 the use of nitrogen on American farms has increased more than ten times. Much of this increase has come in the form of inorganic nitrogen, with synthetic ammonia playing an important role since about 1925. The steadily decreasing cost of fertilizer nitrogen and the increasing price differential in favor of the mineral and synthetic forms appear to have been largely responsible both for the rapidly increasing use of fertilizer nitrogen and for the dramatic shift from organic to mineral.

These changes are the most significant occurrences noted in the use of nitrogenous fertilizers during the past half-century. They are clearly set out in data quoted by Parker[17] and reproduced in part in Table 62.

TABLE 62. USE OF FERTILIZER NITROGEN OF AMERICAN FARMS (1900 TO 1944)

Year	Nitrogen Consumption tons	Part Supplied as Chemical Nitrogen %	Average Wholesale Price of 20 lb. of Nitrogen as -	
			Natural Organics dollars	Chemical Nitrogen dollars
1900	62,000	12	2.57	2.42
1910	145,900	46	3.63	2.76
1920	227,800	66	8.71	4.26
1930	376,600	84	4.50	2.14
1940	419,100	88	3.55	1.42
1944	626,200	94	4.82	1.40

These data show a steadily increasing use of fertilizer nitrogen from 62,000 tons in 1900 to 626,000 tons in 1944. Along with this increased use of nitrogen there has been an equally significant increase in the importance of the part played by the chemical or inorganic form—from 12 per cent of the total in 1900 to 94 per cent in 1944.

In 1900 the price of a unit of nitrogen in the form of organic materials was about the same as that of a unit of chemical nitrogen. Since that time, however, the differential in favor of chemical nitrogen has steadily increased until in 1944 a unit of organic nitrogen cost more than three times as much as a unit of chemical nitrogen.

Mehring[10] emphasizes relative price as the dominant factor determining the choice between the large number of fertilizer materials usually available as sources of nitrogen. Other important factors given by Mehring are chemical properties, physical properties, residual effect on the soil and salesmanship.

Data, taken from Mehring's discussion and indicating the relative importance of various nitrogenous fertilizer materials used both in mixed fertilizer and for direct application during the period of 1880 to 1942, are given in Table 63.

TABLE 63. USE OF NITROGEN IN VARIOUS FORMS IN MIXED FERTILIZERS AND AS SEPARATE MATERIALS

	Solid Nitrate		Solid Ammonium Salts		Natural Organics		Synthetic Organics		Solutions		Total	
Year	Mixed %	Separate %	Mixed %	Separate %	Mixed %	Separate %	Mixed %	Separate %	Mixed %	Separate %	Mixed %	Separate %
1880	0.9	1.4	1.3	0.9	42.4	53.1	-	-	-	-	44.6	55.4
1890	2.9	2.6	0.4	0.2	42.7	51.2	-	-	-	-	46.0	54.0
1900	3.4	7.7	1.0	0.4	44.9	42.6	-	-	-	-	49.3	50.7
1910	7.1	17.0	8.0	13.4	33.6	20.2	0.9	-	-	-	49.6	50.4
1920	8.1	16.9	9.8	30.1	22.0	11.8	1.1	0.2	-	-	41.0	59.0
1925	10.3	28.8	13.2	17.7	16.5	8.9	4.7	0.1	-	-	44.7	59.3
1926	8.2	26.4	16.8	19.6	15.4	8.4	4.9	0.3	-	-	45.3	54.7
1927	5.8	26.5	22.1	18.0	12.1	11.2	5.0	0.4	-	-	45.0	55.0
1928	5.9	27.1	21.2	22.4	11.4	5.6	5.0	0.6	1.0	-	44.5	55.5
1929	5.6	27.1	20.7	18.7	10.3	6.3	4.2	1.4	5.7	-	46.5	53.5
1930	5.0	25.3	20.5	19.4	9.5	6.5	3.7	2.4	7.6	-	46.3	53.7
1931	4.6	23.5	22.7	17.7	8.8	11.1	3.9	1.1	6.6	-	46.6	53.4
1932	4.0	13.7	24.3	25.9	9.8	15.3	4.0	0.9	6.1	-	48.2	51.8
1933	3.5	15.8	26.7	22.7	10.3	10.6	4.0	0.8	5.6	-	50.1	49.9
1934	4.3	19.3	26.6	18.1	10.4	8.5	3.9	2.0	7.6	-	52.8	47.2
1935	4.7	26.7	26.3	11.6	9.6	7.1	3.7	2.5	7.8	-	52.1	47.9
1936	4.6	30.5	27.2	6.5	8.5	8.1	3.4	2.6	8.2	0.2	51.9	48.1
1937	4.2	32.3	28.3	6.5	7.2	5.2	3.8	3.0	8.7	0.7	52.3	47.7
1938	4.3	30.1	24.7	9.9	7.4	5.4	4.3	2.2	10.9	0.8	51.6	48.4
1939	4.5	29.3	24.3	10.5	8.0	4.3	4.7	2.5	12.0	0.9	52.5	47.5
1940	4.8	27.4	20.1	14.5	7.6	4.0	4.5	3.5	12.4	1.2	49.4	50.6
1941	3.5	28.1	17.5	15.0	7.7	2.9	4.5	4.3	16.1	0.4	49.3	50.7
1942	4.3	22.0	28.6	15.0	8.3	2.7	3.3	0.7	14.4	0.7	58.9	41.1

Mehring's data show clearly the long established policy of the American farmer of using approximately one-half of his nitrogen in the form of mixed fertilizer and one-half in the form of separate materials applied directly to his crops. Also shown is the steady decline in natural organics from a dominant position in the period of 1880 to 1900 to a relatively unimportant place during recent years. Along with this decline in the use of natural organics has come an equal increase in the relative proportion of nitrogen derived from inorganic materials, chiefly ammonium salts and solution in mixed fertilizers and nitrates for direct application as separate materials.

The decline in the relative importance of natural organics as fertilizer materials and the shift from seed meals and animal products to other types of materials, such as sewage sludge and process tankage, is shown in data published by Clark and Bear[4] and reproduced in part in Table 64. These data show a surprisingly constant quantity of nitrogen derived from

Table 64. Natural Organics Used in the Manufacture of Mixed Fertilizers

Materials	Tonnage of Material – Short Tons						Equivalent Nitrogen
	1900	1909	1919	1929	1939	1944	1944
Seed meals[1]	151,000	367,000	269,000	197,000	136,000	130,000	7,900
Animal products[2]	209,000	227,000	300,000	158,000	95,000	9,000	800
Process tankage	-	-	10,000	126,000	93,000	105,000	8,700
Garbage tankage	103,000	150,000	116,000	110,000	31,000	15,000	450
Sewage products	-	-	-	24,000	57,000	115,000	6,000
Manures	-	-	33,000	29,000	35,000	25,000	750
Plant materials[3]	10,000	15,000	61,000	103,000	145,000	145,000	2,800
Peat	-	10,000	25,000	40,000	40,000	40,000	600
Total	473,000	769,000	814,000	787,000	632,000	584,000	28,000
Equivalent N	32,300	42,000	49,200	36,300	31,100	28,000	28,000

[1] Apricot seed meal, castor pomace, cottonseed meal, hempseed meal, linseed meal, rape seed meal, soybean meal, tung meal, etc.

[2] Animal tankage, dried blood, fish scrap, hoof and horn meal, and miscellaneous organics.

[3] Cocoa by-products, peanut hull meal, and tobacco stems.

natural organics from 1900 through 1944, a period during which the use of chemical nitrogen increased more than 100 times.

Secondary Effects of Nitrogenous Fertilizer

In addition to their primary purpose of supplying nitrogen to growing crops, nitrogenous fertilizers also often exert important secondary influences on plant growth and bring about pronounced changes in the physical, chemical and biological properties of soils. These secondary influences on plant and soil differ greatly for different materials and may be either beneficial or harmful. They often play a dominant part in determining a choice between several different materials otherwise approximately equally well suited to serve a particular need.

The more important of the secondary effects resulting from the use of nitrogenous fertilizers are due to:

1. Other elements supplied as components of the compounds containing the nitrogen or as impurities in nitrogenous fertilizer materials.
2. Residual effect on soil reaction as a result of the nitrification process in the soil or differential utilization of acidic and basic components of nitrogenous materials.

To be suitable for fertilizer use nitrogen must be combined with other elements to form more or less stable compounds. These other elements that are a part of the nitrogen compounds are many and vary in character and in their effect on plant growth and soil properties.

In so far as plant growth is concerned, they may have little or no direct effect; they may have pronounced direct effects, either favorable or unfavorable without playing an essential role; or they may even be necessary plant nutrient elements. The group that serves as essential plant nutrient elements is especially important and includes elements like potassium, calcium, and sulfur.

Secondary effects on soil properties other than soil reaction are due principally to bases, such as sodium, potassium, and calcium, that remain in the soil. Many of the chemical and physical properties of soils are due to the relative proportions of such bases adsorbed on the colloidal complex. A high proportion of sodium, for example, increases dispersion while replacement of sodium with calcium brings increased flocculation.

The effects of nitrogenous and other fertilizer materials on soil reactions have been studied intensively by Pierre[19, 20, 21] and others. Both observations and experiment have shown clearly that the long continued use of nitrogenous fertilizers or their use in large quantities brings about important changes in soil reaction. These changes may be toward increased acidity, as with ammonium sulfate and other ammonia compounds, or toward decreased acidity, as in the case of most nitrates.

Most nitrogenous fertilizer materials are neutral salts that exhibit little or no characteristics of either acids or bases. Such effects on the soil develop only after the materials have been in the soil for a considerable time and especially in the course of their utilization by crops. These effects on the soil are thus often referred to as "residual" effects; and nitrogenous fertilizers are said to possess properties of "potential acidity" or "potential basicity."

Values for potential acidity and potential basicity are commonly expressed in terms of "pounds, calcium carbonate equivalent." Such values for a number of the more important nitrogenous fertilizer materials are shown in Table 65.

The acidic or basic residual effects of nitrogenous fertilizer result very largely from the preferential intake by crops of one element over another and from the conversion of nitrogen to other forms through nitrification processes in the soil.

Sodium nitrate serves as a good example of the effects of preferential absorption by crops. The acidic nitrate ion is utilized to a greater extent than is the basic sodium ion. The excess sodium ion thus left in the soil serves as a neutralizer for other acidic ions already in the soil and so results in decreased acidity or increased alkalinity.

With materials that undergo nitrification, the nitrogen is converted into the acidic nitrate ion. This acidic nitrate ion then serves as a neutralizer for soil bases and so results in increased soil acidity or reduced alkalinity.

In the case of ammonium salts, like ammonium sulfate, there is a double acidifying effect. The basic ammonium ion is converted by nitrification into the acidic nitrate ion and both this and the residual acidic sulfate ion react with soil bases.

Table 65. Nitrogen Content and Equivalent Acidity or Basicity of Nitogenous Fertilizer Materials

Material	Nitrogen Content %	Calcium Carbonate Requirement or Equivalent			
		Per Unity Nitrogen		Per ton Material	
		Acidity [lb.]	Basicity [lb.]	Acidity [lb.]	Basicity [lb.]
Ammonium nitrate	32.5	36	-	1170	-
Ammonium sulfate	20.5	107	-	2200	-
Ammo-phos	11.0	100	-	1100	-
Anhydrous ammonia	82.2	36	-	2960	-
Aqua ammonia	24.6	36	-	892	-
A-N-L compound	20.5	0	-	0	-
Blood [dried]	13.0	35	-	456	-
Calcium nitrate	15.0	-	27	-	406
Cal-nitro	20.5	0	-	0	-
Castor pomace	4.8	18	-	86	-
Cocoa shell meal	`2.7	-	12	-	32
Cocoa tankage	2.5	-	240	-	600
Cottonseed meal	6.7	28	-	188	-
Aero-cyanamid	22.0	-	57	-	1254
Fish scrap	9.2	18	-	166	-
Guano [Peruvian]	13.8	19	-	262	-
Guano [Whale]	9.7	9	-	88	-
Milorganite	7.0	34	-	388	-
Nitrogen solution	40.8	36	-	1474	-
Nitrogen solution	40.8	36	-	1470	-
Nitrogen solution	37.0	36	-	1332	-
Potassium nitrate	13.0	-	36	-	468
Sodium nitrate	16.0	-	36	-	576
Spensol	40.6	36	-	1464	-
Spensol	40.8	36	-	1470	-
Spensol	37.0	36	-	1332	-
Tankage [animal]	9.0	3	-	27	-
Tankage [garbage]	2.5	-	54	-	134
Tankage [process]	7.5	31	-	232	-
Tobacco stems	2.8	-	86	-	220
Urea	46.6	36	-	1678	-
Urea-ammonia liquor	45.5	36	-	1640	-
Urea-ammonia liquor	37.0	36	-	1332	-

Classification of Nitrogenous Fertilizer Material

Commercial nitrogen for fertilizer use is derived from a wide variety of materials. These materials differ widely in the sources from which they are derived; in the methods by which they are produced; and in their physical, chemical and agronomic properties. They contain nitrogen that is present in many different forms of chemical combination and differs markedly in solubility and availability.

Nitrogenous fertilizers may be readily divided into groups on the basis of the source from which they are derived or the method by which they are produced or on the basis of any of their physical, chemical, and agronomic properties. Many such schemes of classification have been proposed and used. All such schemes serve desirable purposes but, to serve the particular needs of this discussion, classification on the basis of the chemical form in which the nitrogen is combined with other elements within the chemical compound seems most advantageous.

It is obvious, for example, that the form of chemical combination with other elements determines many important properties of the nitrogen and so is most helpful as a basis for discussing such properties. It also is true that this system lends itself to a simple scheme that is easily followed and readily understood.

On this basis, the important nitrogenous fertilizers may be divided into five groups. This grouping, with examples of the more important materials represented by each group, is as follows:

1. **Nitrate**	Sodium nitrate Potassium nitrate Calcium nitrate Nitrate of soda-potash
2. **Ammonia**	Ammonium sulfate Ammonium phosphate Ammonium chloride Free ammonia
3. **Nitrate and Ammonia**	Ammonium nitrate
4. **Amide**	Calcium cyanamide Urea
5. **Protein**	Animal tankage Dried blood Fish scrap Cottonseed meal Castor pomace Process tankage Sewage sludge Tobacco stems

Group 1. Nitrates are obtained both as natural products from salt deposits and as manufactured products made in synthetic ammonia plants. As a class nitrates are characterized by their ready solubility and by their free movement in the soil moisture.

Nitrogen in the nitrate form is more readily and more rapidly utilized by most crops than is nitrogen in any other form. This is one of the chief reasons why nitrates have found such high favor for use as top-dressers and side-dressers and for similar purpose where immediate response and ready penetration of the soil is desired.

Nitrate nitrogen, however, is more subject to leaching losses as a result of heavy rains than are other forms of nitrogen. This is due partly to the ready solubility of this form of nitrogen but primarily to the fact that it is not held or "fixed" by the constituents of the soil to as great an extent as are other forms.

Secondary influences on plant growth and soil properties also are important considerations in the use of nitrate nitrogen. These secondary influences are due chiefly to the fact that most nitrates are salts of nitric acid and strong bases, such as sodium, potassium, and calcium.

All such nitrate materials are potentially basic in their residual effect on the soils and their use may play a significant role in reducing soil acidity. Sodium nitrate, for example, has a potential basicity of 36 pounds, calcium carbonate equivalent, per unit of nitrogen.

Group 2. Free ammonia and compounds having their nitrogen in the ammoniacal form account for a large part of the total fertilizer nitrogen used at the present time. This especially is true for nitrogen used in the form of mixed fertilizers.

Ammonia is obtained both as a by-product from the destructive distillation of coal and from synthetic ammonia plants where it is produced by combining hydrogen with nitrogen taken from the air. It is used both as free ammonia and as fixed ammonia in the form of various salts but especially the sulfate.

Materials having their nitrogen in the form of ammonia, like the nitrates, are readily soluble in water and readily available. Ammoniacal nitrogen, however, is considered to be somewhat less rapidly utilized by growing crops than is nitrate nitrogen and is much more resistant to loss by leaching. This resistance to leaching, in spite of high water solubility, is due to the fact that the ammonium ion, like other positive ions, is readily adsorbed on the colloidal complex of the soil. Ions so fixed are not readily lost by leaching.

Ammoniacal nitrogen can be utilized directly by plants. In practice, however, the greater part of it usually is first changed to the nitrate form through the action of nitrifying bacteria in the soil and absorbed in this form by growing crops.

Group 3. Compounds containing nitrogen in both the ammoniacal and the nitrate form are limited in number. The most important example is ammonium nitrate, a compound that has its total nitrogen content equally divided between the two forms and that is oxidized in the soil to form nitric acid as the only residual product.

Compounds in this group are readily soluble in water and suited to use under a wide variety of soil and cropping conditions. Their nitrogen has the characteristics that would be expected of a combination of the two forms—the nitrate makes for rapid utilization by growing crops and the ammoniacal, to resistance to losses by leaching.

Group 4. The amide form of nitrogen for fertilizer use is limited to synthetic compounds, principally urea and calcium cyanamide. These materials are carbon compounds and so technically are classed as organic. However, they are simple substances produced from simple inorganic materials and their behavior and general composition in many ways bear a closer resemblance to the behavior and composition of inorganic compounds than to organic.

The relatively low price at which amide nitrogen is sold, its ready solubility in water, the ease with which it is decomposed in the soil, and the rapidity with which it is used by crops have brought about the rather general practice of its classification as inorganic or mineral. Amide nitrogen is so classified by many state fertilizer laws or by rules and regulations promulgated under such laws.

Amide nitrogen is nonproteid in character and in general behavior closely resembles the ammoniacal form. In the soil it is easily and quickly changed to ammoniacal nitrogen and thence to nitrate.

Group 5. Animal and vegetable materials, such as animal tankage, dried blood, cottonseed meal, and castor pomace, are commonly referred to as organic ammoniates. The nitrogen contained in such materials is combined in the form of complex organic compounds, mostly proteins. Such nitrogen is largely insoluble in water and relatively slowly available to crops.

Water insoluble, proteid nitrogen of this character cannot be utilized directly by plants. It first must be converted through the processes of decay into simpler and more soluble forms. The end product of these processes in the soil usually is nitrate.

Some organic ammoniates like cottonseed meal and dried blood are broken down rapidly by biological action in the soil and so have their nitrogen quickly changed over into the ammoniacal and nitrate forms. Others, such as hoof meal and ground leather, are so resistant to decomposition in the soil that they are almost never used as fertilizers until they first have been processed to render their nitrogen more readily available.

PRODUCTION OF NITROGENOUS FERTILIZERS

Leading prewar producers of fertilizer nitrogen were Germany, Chile, Japan, and the United States. Data published by Clark and Sherman[5] and reproduced in part in Table 66 show that Germany was by far the largest producer with a production slightly in excess of the combined production of Chile, Japan, and the United States.

Germany also was the largest consumer of nitrogen with the United States, Japan, and France following in that order. German consumption was nearly twice that of the United States, more than twice that of Japan, and nearly four times that of France.

TABLE 66. PREWAR FERTILIZER NITROGEN PRODUCTION IN FOUR LEADING COUNTRIES

	1935 Tons N	1936 Tons N	1937 Tons N	Average Tons N
Germany	653,960	683,790	693,355	677,035
Chile	212,828	236,006	230,838	226,557
Japan	116,358	225,439	243,622	211,808
United States	226,429	183,990	211,874	207,432

In spite of the large consumption, German production was sufficient to take care of all home needs and to provide considerable surplus material for export. Other leading export countries were Chile, Norway, the United Kingdom, and Manchuria, with Chile accounting for a large part of the total volume.

World War II brought profound changes in the nitrogen production picture. War demands led to sharp expansion of production facilities throughout most of the world and especially in the United States and Canada. This American expansion, coupled with war damage to European facilities, has resulted in a shift of the nitrogen production center from Europe to America.

In the United States, for example, data published by Parker et al.[18] and reproduced in Table 67 show an annual production capacity for 1944 of slightly more than 1.5 million tons of chemical nitrogen. This capacity represents approximately a tenfold increase over 1925 and a threefold increase over 1940.

TABLE 67. U. S. CAPACITY FOR PRODUCTION OF CHEMICAL NITROGEN

Year	By-product Tons N	Synthetic Tons N	Total Tons N
1925	147,500	15,300	162,800
1930	194,500	195,500	390,000
1935	185,000	341,350	526,350
1940	185,000	380,300	565,300
1944	225,000	1,285,100	1,510,100

Present United States production capacity for chemical nitrogen is represented by 114 plants, 95 of which produce by-product nitrogen and 19, synthetic materials. The 19 synthetic plants represent more than five-sixths of the total capacity.

Production of by-product nitrogen is dependent on the coke industry which, in turn, is limited by the demands for iron and steel. Ammonium sulfate, the principal material produced, goes very largely to the fertilizer trade.

Synthetic nitrogen, on the other hand, is geared directly to the market demand for nitrogen compounds. A large part of the synthetic nitrogen production finds its way into industrial uses and so is not available to the fertilizer trade.

Description of Nitrogenous Fertilizer Materials

A large number of nitrogenous materials are in common use in the compounding of mixed fertilizers. Many of these same materials are used by farmers for direct application.

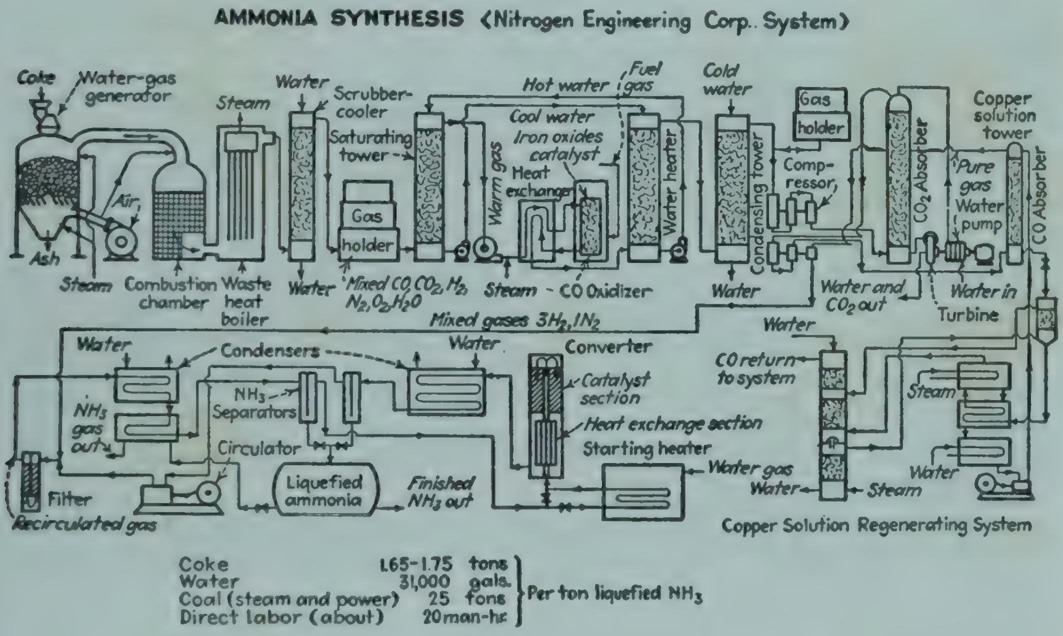
AMMONIA SYNTHESIS (Nitrogen Engineering Corp. System)
Coke
Water-gas generator
Air
Ash
Steam
Combustion chamber
Waste heat boiler
Water
Scrubber-cooler
Saturating tower
Gas holder
Mixed CO, CO2, H2, N2, O2, H2O
Warm gas
Hot water
Fuel gas
Cool water
Iron oxides catalyst
Heat exchanger
Steam - CO Oxidizer
Water heater
Cold water
Condensing tower
Gas holder
Compressor
CO2 Absorber
Copper solution tower
Pure gas
Water pump
CO Absorber
Water and CO2 out
Water in
Turbine
Mixed gases 3H2, 1N2
Condensers
NH3 gas out
NH3 Separators
Circulator
Filter
Recirculated gas
Liquefied ammonia
Finished NH3 out
Converter
Catalyst section
Heat exchange section
Starting heater
Water gas
CO return to system
Copper Solution Regenerating System
Coke 1.65-1.75 tons
Water 31,000 gals.
Coal (steam and power) 25 tons
Direct labor (about) 20 man-hr.
Per ton liquefied NH3

FIG. 4. Flow sheet of ammonia synthesis.

A few of these nitrogenous fertilizer materials are relatively new products but the majority are well known and have been in use over a long period of years. All materials, under normal conditions, have been available in abundant supply so that both the farmer and the fertilizer producer could have complete freedom to choose the ones best suited to fill his own particular needs. Shortages and restricted choice have come only with wars or other abnormal conditions that have brought greatly increased demands and, at the same time, restricted production.

The production, properties, and uses of a wide variety of nitrogenous materials have been discussed by Bear,[2] Blair,[3] Collings,[6] Merz,[11] Moore,[15] Shreiner, Merz and Brown,[24] and by many other workers. An understanding of the properties of the individual materials is necessary before either the farmer or fertilizer producer can make a wise decision regarding their use.

Ammonia. Pure ammonia is a gas made up of 82.25 per cent nitrogen and 17.75 per cent hydrogen. It is the most concentrated and lowest priced nitrogenous material so far used either in the production of mixed fertilizer or for direct application.

Formerly, most of the ammonia used in the United States was obtained as a result of the destructive distillation of coal in by-product coke ovens. In recent years the larger part of our supply has been produced in synthetic ammonia plants where nitrogen and hydrogen are caused to combine chemically to form ammonia (see Figures 4, 5, and 6).

FIG. 5. Aerial view of Synthetic Ammonia Plant at Hopewell, Va. (Courtesy The Barrett Div., Allied Chem. and Dye Corp.)

Commercial ammonia for fertilizer use comes principally in two forms—anhydrous ammonia and aqua ammonia. Both are used extensively in the ammoniation of superphosphate and of fertilizer mixtures and less extensively for direct application to the soil.

Anhydrous ammonia is produced by compressing dry ammonia gas to form a liquid. In this form it is shipped to fertilizer factories in high-pressure tank cars. At the factory it may be introduced directly into the superphosphate or fertilizer mixture in the form of anhydrous ammonia gas or it may first be dissolved in water to form ammoniating solutions of the desired strength.

The fertilizer grade of anhydrous ammonia contains approximately 99.5 per cent ammonia, equivalent to 82 per cent nitrogen. It is acid forming and has a potential acidity of 148 pounds, calcium carbonate equivalent, per 100 pounds of material or 36 pounds per unit of nitrogen.

Aqua ammonia is formed by dissolving ammonia gas in water. Commercial grades of aqua ammonia prepared for fertilizer use usually contain approximately 30 per cent ammonia.

Aqua ammonia is widely used both alone and in combination with other nitrogenous materials for the ammoniation of superphosphate and fertilizer mixtures. Like anhydrous ammonia it is acid-forming and has a potential acidity of 36 pounds, calcium carbonate equivalent, per unit of nitrogen.

FIG. 6. Ammonia synthesis—42-inch gas lines as they leave the gas reforming plant carrying the reformed gas to the ammonia plant. (Courtesy Spencer Chem. Co.)

So far both anhydrous and aqua ammonia have been used largely in the fertilizer factory for ammoniating superphosphate and fertilizer mixtures. However, considerable experimental work looking toward use in direct application has been carried on with some favorable results that promise more extensive use. Examples of such results are the use of anhydrous ammonia for introduction into irrigation water in California and other western states and for direct application to the soil in the Delta region of Mississippi [1] (see Figure 7).

Ammoniating Solutions. Ammoniating solutions are concentrated water solutions of free ammonia in which are dissolved fixed nitrogen compounds, such as ammonium nitrate and urea. These solutions are used extensively in the ammoniation of both superphosphate and mixed fertilizers and have become one of our most important sources of fertilizer nitrogen.

The use of ammoniating solutions largely overcomes the problem presented by the low proportion of nitrogen that can be added to superphosphate and to fertilizer mixtures through the use of anhydrous or aqua ammonia. Ammoniating solutions have only approximately one-half of their total nitrogen in the form of neutralizing ammonia and so can be used to supply twice as much total nitrogen without increasing the danger of loss of available phosphoric acid because of reversion.

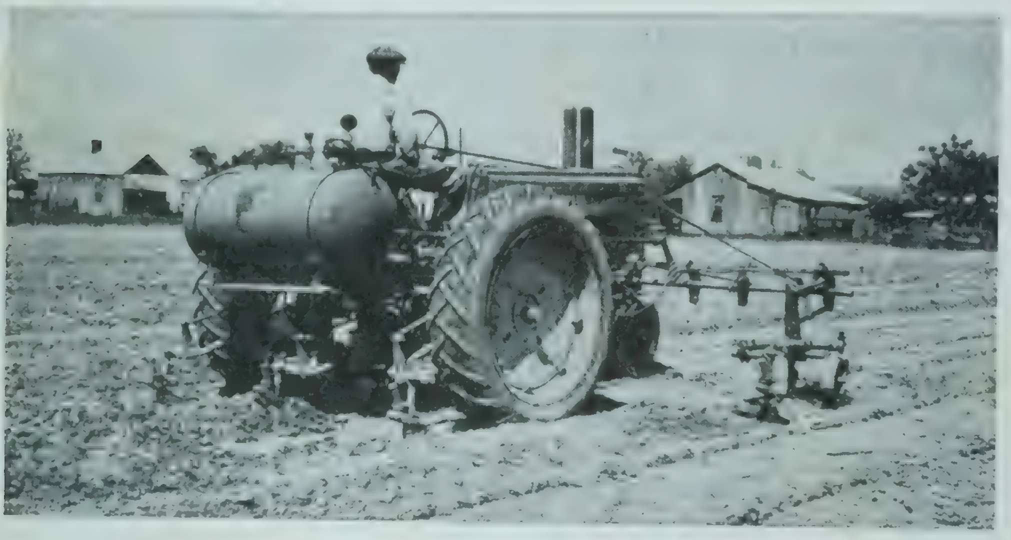

FIG. 7. Applying anhydrous ammonia directly to the soil. (Courtesy Miss. Agr. Expt. Sta.)

A number of different ammoniating solutions have been extensively used by the fertilizer industry. These solutions have been marketed in the United States principally under trade names, such as *Nitrogen Solution*, *Spensol*, and *Urea-Ammonia Solution*, several solutions varying somewhat in composition and concentration usually being offered under each general trade name.

Ammoniating solutions now in general use in the United States may be divided into two classes:

1. Solutions containing ammonium nitrate as the fixed nitrogen compound.
2. Solutions containing urea as the fixed nitrogen compound.

Materials sold under the trade name *Nitrogen Solution* and *Spensol* are examples of class 1, whereas *Urea-Ammonia Solution* is an example of class 2. Data showing the general composition of these ammoniating solutions are given below.

Barrett Nitrogen Solution 2A, Spensol A, and Lion Nitrogen Solution 1 contain 65.0 per cent ammonium nitrate, 21.7 per cent anhydrous ammonia, and 13.3 per cent water, giving a ratio of free to fixed nitrogen of 1 to 1.27. The total nitrogen content is 40.6 per cent, of which 28.0 per cent is in the nitrate form and 72.0 per cent in the form of free and combined ammonia. When using these solutions, 1.27 per cent of nitrogen in the form of ammonium nitrate is added for each 1 per cent added as free ammonia.

Barrett Nitrogen Solution 3, Spensol B, and Lion Nitrogen Solution 2 are made up of 55.5 per cent ammonium nitrate, 26.0 per cent anhydrous ammonia and 18.5 per cent water, giving a ratio of free to fixed nitrogen of 1.0 to 0.90. They have a total nitrogen content of 40.8 per cent, of which 23.6 per cent is in the nitrate form and 76.4 per cent in the form of free and combined ammonia. With these solutions there is added 0.90 per cent nitrogen in the form of ammonium nitrate for each 1 per cent added as free ammonia.

Barrett Nitrogen Solution 4, Spensol C, and Lion Nitrogen Solution 3 contain 66.8 per cent ammonium nitrate, 16.6 per cent anhydrous ammonia, and 16.6 per cent water, giving a ratio of free to fixed nitrogen of 1 to 1.7. They have a total nitrogen content of 37.0 per cent, of which 31.5 per cent is in the nitrate form and 68.5 per cent in the form of free and combined ammonia. Using these solutions gives 1.7 per cent of nitrogen in the form of ammonium nitrate for each 1 per cent as free ammonia.

Urea-Ammonia Liquors in five different types and concentrations, designated as *A, B, C, D,* and *37* have been produced and used in large quantities for a number of years. The composition of the five solutions making up this group is as follows:

	UAL–A	*UAL–B*	*UAL–C*	*UAL–D*	*UAL–37*
Nitrogen as urea (%)	15.1	20.2	12.3	16.4	9.1
Nitrogen as ammonia (%)	30.4	25.3	24.7	20.6	20.6
Nitrogen as water insoluble (%)	—	—	—	—	7.4
Water (%)	24.8	17.6	38.6	32.8	24.8
Ratio—fixed to free nitrogen	0.5–1.0	0.8–1.0	0.5–1.0	0.8–1.0	0.8–1.0

Urea-Ammonia Liquors C and *D* are dilute solutions of *A* and *B* and so contain the same relative proportions of fixed and free nitrogen. *Urea-Ammonia Liquor 37* differs from the others in that, when mixed with superphosphate, it supplies a part of its total nitrogen in the water insoluble form through the production of ureaformaldehyde compounds.

Ammoniated Superphosphate. The process for the treatment of superphosphate with free ammonia is the outstanding development in the fertilizer industry during recent years. The product resulting from this treatment, called ammoniated superphosphate, has found wide use both in the preparation of mixed fertilizers and for direct application.

In commercial practice the free ammonia may be added in the form of anhydrous ammonia, aqua ammonia, or one of the several ammoniating solutions consisting of a water solution of free ammonia in which other nitrogen compounds have been dissolved. The superphosphate may be either the usual grade containing 18 to 20 per cent phosphoric acid (P_2O_5) or the concentrated form with a phosphoric acid (P_2O_5) content of 45 to 50 per cent and it may be ammoniated as a separate material or in combination with the other materials that go to make up the mixed fertilizer.

When the free ammonia comes in contact with the superphosphate it immediately reacts with any free acid present and with other acidic phosphates to form fixed ammonium compounds. The two materials thus combine chemically to give a mixture made up essentially of monoammonium phosphate, dicalcium phosphate, tricalcium phosphate, ammonium sulfate, and gypsum.

The principal reaction involved in the ammoniation of ordinary superphosphate, as given by Keenen,[8] are as follows:

$$CaH_4(PO_4)_2 + NH_3 \rightarrow NH_4H_2PO_4 + CaHPO_4$$

$$2CaHPO_4 + CaSO_4 \cdot 2H_2O + 2NH_3 \rightarrow (NH_4)_2SO_4 + Ca_3(PO_4)_2 + 2H_2O$$

$$CaH_4(PO_4)_2 + 2NH_3 \rightarrow CaHPO_4 + (NH_4)_2HPO_4$$

$$NH_4H_2PO_4 + CaSO_4 \cdot 2H_2O + NH_3 \rightarrow (NH_4)_2SO_4 + CaHPO_4 + 2H_2O$$

From the above reactions it will be seen that in the ammoniation process a part of the monocalcium phosphate is changed to dicalcium and tricalcium forms. This change, known as reversion, increases with increased additions of ammonia and results in considerable loss of available phosphoric acid with high rates of ammoniation.

Ordinary superphosphate will absorb up to 6 per cent free ammonia and concentrated superphosphate proportionately more. In such completely ammoniated superphosphate the greater part of the phosphoric acid is found in the form of tricalcium phosphate and nearly all of the ammonia, in the form of ammonium sulfate.

In practice loss of available phosphoric acid through reversion makes it uneconomical to carry the ammoniation process much beyond the halfway point. Tricalcium phosphate formation increases rapidly with ammonia additions above the 3 per cent level for ordinary superphosphate.

Regardless of the ammoniating material used, the free ammonia is the active ingredient and the free ammonia content determines the quantity that can be used per ton of superphosphate. Dissolved nitrogen salts play little or no important part in the reactions but do make it possible to produce a product with a higher nitrogen content without danger of reversion due to over-ammoniation.

Ammoniated superphosphate is a desirable product primarily because it makes possible the direct use of free ammonia, the fertilizer industry's cheapest and most concentrated source of nitrogen. In addition, ammoniation makes for a reduced free acid content, more rapid curing, and improved mechanical condition.

Ammonium Nitrate. Pure ammonium nitrate is a white crystalline salt usually prepared by neutralizing ammonia with nitric acid. It has a nitrogen content of 35 per cent, one-half of which is present in the ammonia form and one-half in the nitrate form. Due to the necessity of adding conditioning agents, the commercial product usually carries a guarantee of only 34.0 per cent nitrogen.

Commercial production of ammonium nitrate for fertilizer use is confined almost entirely to synthetic ammonia plants. Ammonia is first oxidized to nitric acid and then a solution of this product is neutralized with gaseous ammonia. The solution of ammonium nitrate resulting from this neutralization is concentrated to a melt by evaporation and then converted into a solid crystalline or granular product by "graining" or "spraying."

Ammonium nitrate has proved to be an excellent fertilizer material both for direct application to the soil and for use in fertilizer mixtures. It is an economical source of fertilizer nitrogen and is suited to a wide range of crops, soils and climatic conditions. Its nitrate nitrogen content contributes to rapid crop response while the ammonia half of the nitrogen makes it more resistant to leaching losses than are materials carrying all their nitrogen in the nitrate form.

Although an excellent material from agronomic and economical standpoints, ammonium nitrate has several undesirable physical and chemical properties. These properties present certain difficulties in commercial handling and transportation and have led to the development of special treatments to make the material more suitable for fertilizer use.

Pure ammonium nitrate is highly hygroscopic and shows a marked tendency to absorb moisture from the air and to cake. This tendency is especially troublesome when the air humidity exceeds 60 per cent at 30° C. (86° F.) and is more pronounced for powdered or finely divided material than for larger crystals or granules.

Several successful processes for treatment to reduce moisture absorption and caking have been developed and put into commercial operation. These processes may vary somewhat in detail but consist, essentially, of coating the crystals or granules with around 5 per cent of a conditioning agent, such as kaolin, keiselguhr, or clay and, in some cases, with 1 per cent or less of one or more water-repellent materials such as wax, grease, or oil. Such treated material then is stored in moisture-proof bags.

Another feature that must be given consideration in the handling and storage of ammonium nitrate is danger from explosion and fire. Ammonium nitrate is explosive, under some conditions, and is looked upon as presenting a somewhat serious fire hazard. Such hazards in the handling and storage of ammonium nitrate, due to the high concentration of nitrate in this material, are greater than those presented by sodium nitrate and other similar compounds. Fortunately the treatment that ammonium nitrate normally receives in the fertilizer plant involves little explosion or fire hazard.

Excellent discussions of the production, properties, and use of ammonium nitrate have been published by Ross et al.[22] and by Whittaker and Mehring [27] as well as by a number of other workers.

Ammonium Nitrate-Limestone Mixtures. Ammonium nitrate, in addition to its use as such, is sold for fertilizer use in the form of mixtures with either high calcium or dolomitic limestone. Some of the trade names under which such mixtures have been distributed are *Nitro-chalk*, *Kalkammonsaltpeter*, *Cal-nitro* and *A–N–L*.

Cal nitro and *A–N–L Brand Fertilizer Compound* are the principal materials of this type distributed and used in America. *Cal-nitro* formerly came entirely from Europe but now is being produced at Hopewell, Va. *A–N–L Brand Fertilizer Compound* likewise is produced in a synthetic ammonia plant at Hopewell, Va.

Both American materials are essentially mixtures of approximately 65 per cent ammonium nitrate and 35 per cent finely ground dolomitic limestone; both carry guarantees of 20.5 per cent nitrogen, one-half of which occurs as ammoniacal nitrogen and one-half as nitrate nitrogen; and both are made into pellet form to give better storage, handling, and drilling qualities. Both materials likewise contain approximately 6.5 per cent calcium and approximately 4.2 per cent magnesium and both are nonacid forming.

Ammonium nitrate-limestone mixtures, such as these, have received their most extensive use for direct application but are used to some extent in the preparation of mixed fertilizers. They are adapted to a wide range of soil and crop conditions, store and handle well, and have approximately the same nitrogen content as other materials that the farmer is accustomed to handle.

Ammonium Sulfate. Ammonium sulfate, better known commercially as sulfate of ammonia, in recent years has replaced nitrate of soda as the favorite solid nitrogen material for use in the production of mixed fertilizers. Prior to our greatly expanded production and use of synthetic ammonia, ammonium sulfate supplied the greater part of the nitrogen used in mixed fertilizer in the United States and was responsible for nearly one-half of the nitrogen used in fertilizers throughout the world.

The production of ammonium sulfate is world-wide, being reported as manufactured by 15 of the leading nations of the world. In addition to its extensive use in mixed fertilizers, large quantities of ammonium sulfate are used for direct application.

By far the greater part of the ammonium sulfate produced in the United States is obtained as a waste product in destructive distillation of coal in by-product coke ovens and in coal gas retorts. The ammonia gas evolved in the distillation process is absorbed in a sulfuric acid solution, crystallized and dried to form the commercial salt, as shown in Figure 8.

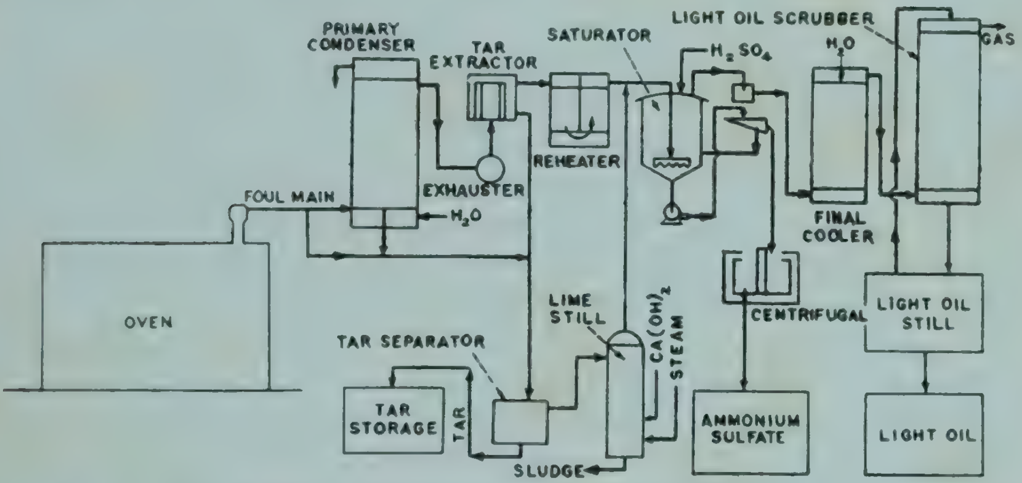
PRIMARY CONDENSER
TAR EXTRACTOR
SATURATOR
LIGHT OIL SCRUBBER
H2SO4
H2O
GAS
REHEATER
EXHAUSTER
FOUL MAIN
H2O
FINAL COOLER
OVEN
LIME STILL
CA(OH)2
STEAM
CENTRIFUGAL
LIGHT OIL STILL
TAR SEPARATOR
TAR STORAGE
TAR
SLUDGE
AMMONIUM SULFATE
LIGHT OIL

FIG. 8. Flow sheet of by-product ammonium sulfate recovery. (Courtesy The Barrett Div., Allied Chem. and Dye Corp.)

In Europe synthetic sulfate of ammonia has been produced on a large scale by a method known as the gypsum process. The essential materials needed in this process are ammonia, pulverized calcium sulfate, carbon dioxide, and water. These materials react to form ammonium sulfate and calcium carbonate as follows:

$$2NH_3 + CaSO_4 + CO_2 + H_2O \rightarrow (NH_4)_2SO_4 + CaCO_3$$

The commercial ammonium sulfate commonly found on the market today is a white or gray salt made up of fine crystals. It is guaranteed to contain 20.5 per cent nitrogen, has a low moisture content and good physical condition and contains little or no free sulfuric acid. It is not hygroscopic under ordinary conditions and will not take up additional moisture if stored in a reasonably dry place.

Ammonium sulfate is strongly acid forming with a potential acidity of 107 pounds, calcium carbonate equivalent, per unit of nitrogen. When used in large quantities without lime or other basic materials it will increase soil acidity to a marked degree. Many unfavorable results from the use of ammonium sulfate have been traced to a lack of recognition of the effect of its continued use on soil reaction.

Ammonium sulfate is readily soluble in water and has proved to be a good source of readily available nitrogen for growing crops. In addition to nitrogen, it contains approximately 24 per cent sulfur, an essential plant food that is now known to be deficient in many soils.

Animal Tankage. The product resulting from the processing of animal waste material obtained from slaughterhouses, butcher shops, dead animals, and various other sources is known as animal tankage. Usually the animal waste is cooked with steam to disintegrate the tissue and to set free the fat, the fat pressed out or skimmed off and the residue dried and ground.

The nitrogen content of animal tankage is highly variable and is dependent principally on the proportion of bone and other low nitrogen materials present. A high-grade tankage contains around 10 per cent nitrogen, but lower grades range all the way down to 5 per cent.

Animal tankage once was a popular fertilizer material but now, due to the higher prices paid for use as a feed, goes largely to the feed trade. It is an excellent source of organic nitrogen in fertilizers.

Calcium Cyanamide. The commercial nitrogenous fertilizer material prepared synthetically by passing pure nitrogen under pressure over heated calcium carbide is known as calcium cyanamide (Figure 9). It is composed chiefly of calcium cyanamide ($CaCN_2$) but also contains considerable quantities of calcium hydroxide and free carbon as well as smaller amounts of other impurities.

Calcium cyanamide has been produced in large quantities in Europe as well as in America and is one of the important nitrogenous fertilizer materials of the world. It has received extensive use both in the preparation of mixed fertilizers and for direct application.

Calcium cyanamide has been marketed under various names, such as *Lime-nitrogen*, *Nitrolime*, and *Cyanamid*. The American product is sold under the trade name of *Aero-cyanamid* and often is spoken of simply as *Cyanamid.*

Aero-cyanamid is produced in both pulverized and granular forms. It comes as a grayish-black powder or pellet and is made up of 60–65 per cent calcium cyanamide, 15 to 20 per cent calcium hydroxide and 10 to 12 per cent free carbon. It is guaranteed to contain 21 to 22 per cent nitrogen, practically all of which is in the water-soluble form.

Calcium cyanamide is strongly alkaline and must be used with great care in the preparation of mixed fertilizers. Used at a rate of 50 to 60 pounds per ton it acts as an excellent drying and conditioning agent. At higher rates excessive heat is likely to be generated and available phosphoric acid lost through reversion.

Experience has shown that calcium cyanamide is toxic to plants and not suited for direct application to all crops or under all soil conditions. It gives best results on the heavier and more acid soils and has been most extensively used on meadows and other grass land. It also has been extensively used for direct application for small grain crops and orchards.

In its residual effect on the soil cyanamid, in contrast to most nitrogenous fertilizers, is basic with a potential basicity of 57 pounds, calcium carbonate equivalent, per unit of nitrogen or 62.5 pounds per 100 pounds of material. This high residual basicity is due to the fact that, in the soil, all calcium contained in the original material is changed to calcium carbonate.

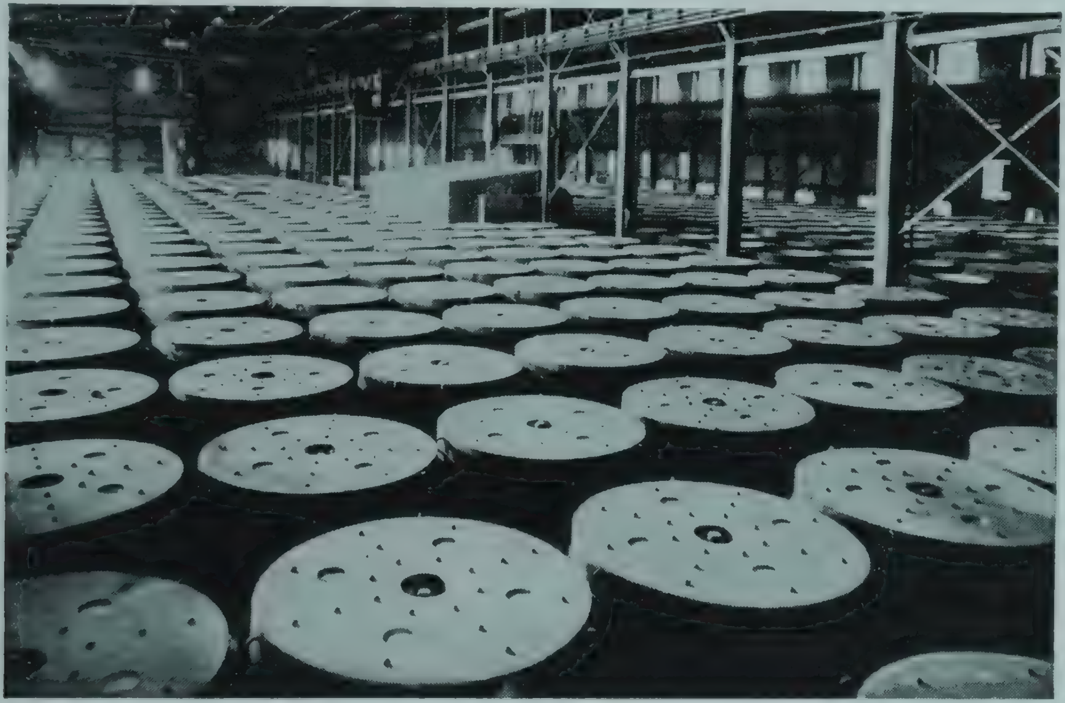

FIG. 9. Ovens in which nitrogen from the air is combined with calcium carbide to form Aero Cyanamid. (Courtesy American Cyanamid Co.)

Calcium Nitrate. Fertilizer grade calcium nitrate has been produced in large quantities in Europe, principally in Norway and Germany, and sold in considerable amounts in the United States. It is made by reacting nitric acid, produced in synthetic ammonia plants, with calcium carbonate or limestone.

Two principal products have been produced, one containing 13.0 per cent nitrogen and the other, 15.5 per cent. The latter material is the one principally sold in the United States. It is essentially a mixture of approximately 95 per cent hydrated calcium nitrate—$Ca(NO_3)_2 \cdot 2H_2O$—and 5 per cent ammonium nitrate. As marketed in the United States this material is granular and carries approximately 1 per cent of its nitrogen in the ammoniacal form and the remainder as nitrate.

From an agronomic standpoint calcium nitrate is an excellent fertilizer material. All of its nitrogen is in the most readily available form and in addition it supplies approximately 24 per cent water soluble calcium, one of the most important of all soil bases and plant nutrient elements. These characteristics make it appear as a nearly perfect material, especially for direct application to growing crops.

On the unfavorable side, however, are the important factors of a relatively low nitrogen content and undesirable physical properties. Calcium nitrate is one of the most hygroscopic of all fertilizer materials. The pure powdered salt absorbs water so readily that it is practically impossible to handle it in a satisfactory manner. Material of the fertilizer grade in granular form is much more easily handled but still must be shipped in moisture-proof containers and applied to the soil without undue delay once the container has been opened.

The residual effect of calcium nitrate on the soil is strongly basic due to the fact that the acidic nitrate ion is utilized more rapidly than is the basic calcium ion. Material of the fertilizer grade described above has a potential basicity of 27 pounds, calcium carbonate equivalent, per unit of nitrogen or 20.3 pounds per 100 pounds of material. The use of calcium nitrate, therefore, is especially effective on acid soils and for crops having a high calcium requirement.

Castor Pomace. Castor pomace is the residue left behind when oil is extracted from the castor bean and thus is a by-product of the castor oil industry. It is poisonous to animals and so is not used as a feed for livestock.

The nitrogen content of castor pomace is somewhat variable but averages about 5.5 per cent. Along with this nitrogen goes 1 to 2 per cent phosphoric acid (P_2O_5) and 1 to 1.5 per cent potash (K_2O).

Castor pomace, because of lack of competition from the feed trade, is lower in price and more generally available for fertilizer use than are most other seed meals. It is extensively used both for direct application and in the preparation of mixed fertilizers. It ranks high as a source of organic nitrogen.

Calurea. *Calurea* is the trade name for a nitrogenous fertilizer material developed and produced in Germany. It is essentially a double salt prepared through the interaction of calcium nitrate and urea. In this interaction four molecules of urea combine with one molecule of calcium nitrate.

Calurea is a white crystalline product that is readily soluble in water.

It contains approximately 34 per cent nitrogen, 80 per cent of which is in the form of urea and 20 per cent, in the form of nitrate.

Cottonseed Meal. The ground residue left when oil is extracted from cottonseed is called cottonseed meal. After the cottonseed is crushed the meats and hulls are separated, the oil extracted from the meats and the residue ground and marketed for use as feed and fertilizer.

The nitrogen content of cottonseed meal varies from 6.0 to 7.5 per cent, the lower nitrogen content usually being due largely to contamination with hulls. In addition to nitrogen it contains approximately 2.5 per cent phosphoric acid (P_2O_5) and 1.5 to 2.0 per cent potash (K_2O) and important amounts of secondary and minor plant nutrient elements, especially magnesium.

Cottonseed meal is in demand as a cattle feed and the greater part of the total production goes for that purpose. Considerable quantities, however, go into the fertilizer trade in certain sections of the country where in spite of its high price it is in demand for use on special high-value crops like tobacco.

Cottonseed meal is used both for direct application and in the preparation of mixed fertilizer. Its nitrogen is largely water insoluble but, under favorable weather conditions, is quickly broken down in the soil and utilized by crops.

Dried Blood. Dried blood is the product obtained when the blood of animals killed in the slaughterhouses is collected, dried, and ground. Dried blood formerly was extensively used as a nitrogenous fertilizer but now, due to the big demand for stock feeding purposes and high prices offered by this trade, little of the product finds its way into the fertilizer factory.

Good quality dried blood has a nitrogen content of from 12 to 14 per cent. Lower qualities may contain as little as 9 per cent nitrogen due to high moisture content and to dilution with other animal products having a lower nitrogen content.

The nitrogen content of dried blood is proteid in character and must be converted into more soluble forms before it can be utilized by plants. In the soil this necessary conversion takes place rapidly so that the nitrogen is considered as readily available.

Dried blood is an excellent source of organic nitrogen and long has been especially prized for greenhouse use. In residual effect it is acid forming with a potential acidity of 35 pounds, calcium carbonate equivalent, per unit of nitrogen.

Fish Scrap (Acidulated). Acidulated fish scrap or acid fish is the product obtained when fish waste is treated with an acid, usually sulfuric, to act as a preservative in holding down decomposition. This material has a high moisture content and a strong and persistent odor.

Formerly, acidulated fish scrap was used in large quantities in the production of mixed fertilizers in certain sections of the United States. At the present time, only a small quantity is produced or used in fertilizers.

The composition of acidulated fish scrap is quite variable but averages about 5.0 per cent nitrogen and 5.0 per cent phosphoric acid (P_2O_5). The nitrogen content is largely in the water insoluble but readily available form.

Fish Scrap (Dried). Dried fish scrap is obtained chiefly from the processing of nonedible fish, like menhaden and dogfish, and waste material from fish canneries. In the rendering process the fish are cooked with steam and the oil pressed out. The residue then is dried, ground and sold under a variety of names, such as "fish scrap," "fish meal," "fish tankage," "dry ground fish," and "fish guano."

The nitrogen content of dried fish scrap will average approximately 8 per cent and the phosphoric acid (P_2O_5) content, about 6 per cent. The nitrogen is organic and proteid in character and largely water insoluble but readily available in the soil.

Dried fish scrap once was a popular fertilizer material but now is little used. Due to scarcity and high price, nearly all of the present production goes to the feed trade.

Garbage Tankage. Garbage tankage is the product obtained when kitchen waste is rendered, dried, and ground. It is a low-grade fertilizer material and is seldom used except as a conditioner in mixed fertilizers and in the production of wet mix "base goods."

The nitrogen content of garbage tankage is low, 2.0–3.5 per cent, and of poor quality because of its slow availability. Small amounts of phosphoric acid and potash also are present.

Mono-Ammonium Phosphate. Mono-ammonium phosphate for fertilizer use is made by mixing together the proper proportions of crude phosphoric acid and ammonia. The crude salt so produced may contain considerable quantities of impurities but is essentially mono-ammonium phosphate.

Fertilizer grade mono-ammonium phosphate has been sold in the United States principally under the trade name *Ammo-phos.* It is almost completely soluble in water and contains 11.0 per cent nitrogen, all of which is in the ammoniacal form, and 48.0 per cent available phosphoric acid.

Mono-ammonium phosphate is a highly concentrated material and is especially well suited for use in the preparation of high analysis mixed fertilizers. It also has found a limited use for direct application.

Nitrate of Soda-Potash. As the name indicates, nitrate of soda-potash is a commercial product made up of a mixture of sodium and potassium nitrates. It is a product of the Chilean nitrate industry and is obtained by refining naturally occurring crude salt or *caliche* containing a high proportion of potassium nitrate.

Nitrate of soda-potash is marketed with guarantees of around 14 per cent nitrogen and 14 per cent potash (K_2O). It has been produced only in limited quantities but has proved to be an excellent material both for direct application and for use in the preparation of mixed fertilizers.

Potassium Nitrate. Potassium nitrate is the potassium salt of nitric acid. It is produced by reacting nitric acid with potassium hydroxide, potassium carbonate or potassium chloride, and by the interaction of potassium chloride and sodium nitrate.

Small deposits of more or less pure potassium nitrate occur in various parts of the world but are of little commercial importance. *Caliche*—the mineral from which sodium nitrate is refined in Chile—contains small amounts of potassium nitrate, usually 2 to 3 per cent, and constitutes the principal source of this material at the present time.

Commercial grades of potassium nitrate previously on the market have contained 12 to 14 per cent nitrogen and 44 to 45 per cent potash (K_2O). All of the nitrogen is in the nitrate form and therefore is readily utilized by plants.

Potassium nitrate is less hygroscopic than most other nitrates used for fertilizer purposes and stays in good physical condition for handling and distribution. It is an excellent material both for direct application and for use in mixed fertilizers.

Process Tankage. Process tankage is the dried and ground product resulting from the treatment of inert organic nitrogenous waste materials with steam under pressure, with or without the use of acids. The materials commonly used in the process are rough ammoniates, such as leather scrap, hair, hoof and horn meal, wool and silk waste, fur, felt, and feathers.

Large quantities of process tankage are used, principally as a source of organic nitrogen in mixed fertilizers. American production is marketed under numerous trade names, such as *Agrinite, Hynite, Nitrolene, Omega, Org-Amo* and *Smirow.*

The nitrogen content of process tankage varies from 6.0 to 10.0 per cent depending largely on the type of raw material from which it is made. This nitrogen is largely water insoluble and relatively slow acting but is considered to be of good quality.

Rough Ammoniates. Organic nitrogenous waste materials, like scrap leather, hair, hoof meal, fur, felt, and wool and silk waste, are known as rough ammoniates. Such materials are high in nitrogen but not suited for fertilizer use until treated to render their nitrogen content more readily available to plants.

Rough ammoniates are used principally in the production of process tankage or else are acidulated along with phosphate rock to produce what is commonly known as "wet base goods." By such treatments these inert materials are transformed into valuable nitrogenous fertilizers.

Sewage Sludge (Activated). Activated sewage sludge is the residue from the purification of city and town sewage by the "activated" process. In this process the raw sewage is freed from grit and coarse solids, inoculated with suitable microorganisms, and aerated. The flocculated organic matter resulting from this treatment is then dried, ground, and screened.

Considerable quantities of dried activated sludge have been produced and used for fertilizer purposes both in Europe and in America. In the United States, for example, it is produced in considerable quantities by the cities of Milwaukee, Pasadena, Houston, and Chicago and in smaller quantities by several other cities.

The nitrogen content of dried activated sewage sludge varies from about 4.0 to 6.5 per cent. There also is a phosphoric acid (P_2O_5) content of around 3.5 per cent. The nitrogen is largely water insoluble and is considered to be of good quality.

Dried sewage sludge has been used extensively as a "specialty fertilizer" for direct application to lawns, flowers, shrubs, and golf courses and as a conditioner and a source of organic nitrogen in mixed fertilizers. It is marketed under various trade names, such as *Milorganite*, *Nitrorganic*, and *Hu-Actinite*.

Sodium Nitrate. Pure sodium nitrate is a white crystalline salt containing approximately 16.5 per cent nitrogen, all of which is in the nitrate form. It is readily soluble in water and rather highly hygroscopic.

Commercial sodium nitrate, better known as nitrate of soda and Chile saltpeter, was the first inorganic nitrogenous material to be used as a fertilizer on a practical scale. Even today, farmers as a whole probably are more familiar with sodium nitrate than with any other nitrogenous fertilizer material.

In the early days the sodium nitrate used for fertilizer purposes came almost entirely from huge deposits located in Chile. Tremendous quantities of this natural product have been mined, processed and sold for fertilizer use over the past 100 years. More recently large quantities of sodium nitrate have been produced in the synthetic ammonia plants and sold in competition with the Chilean product.

Small natural deposits of sodium nitrate have been found in many parts of the world but the only such deposit so far proven to be of any great commercial importance is located in Chile. This deposit is located in the desert land of Tarapaca Plateau and contains known reserves of over 200,000,000 metric tons.

The sodium nitrate in the Chilean deposits occurs as part of a rather complex salt mixture, along with varying amounts of potassium nitrate; sodium, calcium and magnesium chlorides and sulfates; and small quantities of iodates and borates. The sodium nitrate content of this mixed salt deposit, called *caliche*, occasionally goes as high as 70 per cent but seldom exceeds 30 per cent in deposits being worked at the present time.

Two methods for refining the natural crude salt mixture or caliche are in use at the present time. The older of these is the Shank's process and the newer, the Guggenheim process. The introduction of the Guggenheim process, beginning about 1926, has materially lowered production cost and has made possible the utilization of much low-grade caliche that could not be worked profitably by older refining processes.

In the Shank's process, the crude caliche or ore is leached with boiling water and the sodium nitrate crystallized by cooling. The finished product in the form of medium sized, rather uniform crystals is guaranteed to contain 16 per cent nitrogen and is sold under the trade name of *Old Style Chilean Nitrate of Soda.*

With the Guggenheim process, the crude ore is leached with warm water and the sodium nitrate crystallized by the use of artificial refrigeration. The crystallized material then is melted and sprayed through nozzles in such a manner that it solidifies into granular or pellet form on cooling. The finished product from the Guggenheim process is distributed under the trade name, *Champion Brand Chilean Nitrate of Soda*, and contains approximately 16.2 per cent nitrogen.

Sodium nitrate from the Chilean deposits, due to its natural origin, contains small quantities of numerous other elements, carried over as impurities from the crude ore. Included in these impurities are a number of important secondary and minor plant nutrient element, such as magnesium, manganese, boron, copper, and zinc.

Synthetic sodium nitrate is produced in large quantities in synthetic ammonia plants both in the United States and in Europe. The principal process used consists essentially of the oxidation of ammonia to nitric acid and the neutralization of the nitric acid so produced with soda ash to give the sodium salt. The resulting solution of sodium nitrate is concentrated by evaporation and the solid salt produced by crystallization.

Synthetic sodium nitrate is produced in the United States at Hopewell, Va., and distributed under the *Arcadian* brand name. The Arcadian product comes in the form of medium sized crystals having rounded edges. It is white in color and contains from 16.00 to 16.25 per cent nitrogen.

Sodium nitrate is one of our principal sources of nitrogen for fertilizer use. Both experience and experimental evidence have shown it to be one of the most efficient and dependable sources of fertilizer nitrogen. All of the nitrogen in sodium nitrate is in the nitrate form, is readily soluble in water and is quick-acting when applied to growing crops.

In addition to its nitrogen, commercial sodium nitrate contains approximately 27 per cent sodium. Although sodium is not considered an essential plant nutrient element, it is known to exert a favorable influence on potassium economy and other phases of plant nutrition. It seems likely that at least a part of the value of sodium nitrate as a fertilizer is due to its sodium content.

Sodium nitrate has a wide use both for direct application and in the preparation of mixed fertilizers. A detailed discussion of the production and agricultural use of this important fertilizer material is given by Merz and Fletcher.[13]

Tobacco Stems. Tobacco stems is the ground waste product obtained in the processing of tobacco for the manufacture of cigarettes, cigars, and chewing and smoking tobaccos. It is made up largely of stalks, stems, and ribs of tobacco leaves.

Most tobacco waste now is processed for removal of nicotine before being marketed. Such processing destroys any virus disease present in the tobacco waste and renders it safe for fertilizer use.

Tobacco stems contain from 1.5 to 4.0 per cent nitrogen and from 4.0 to 10.0 per cent potash (K_2O). The nitrogen is present partly in the organic form and partly as nitrate.

Tobacco stems is used primarily in the preparation of mixed fertilizers where it serves as an excellent conditioner in addition to supplying nitrogen and potash.

Urea. When ammonia and carbon dioxide are brought together under high pressure and other suitable conditions they combine to form urea. This product is a white crystalline compound that is being produced synthetically on a large scale in both Europe and America.

Commercial urea is relatively pure and contains approximately 46 per cent nitrogen. The use of conditioning agents, however, results in nitrogen guarantees as low as 40 per cent for some of the urea fertilizer products.

In the United States urea for fertilizer purposes has been marketed principally under the trade names, *Ureor* and *Uramon*. *Ureor* fertilizer formerly was imported from Europe and sold under a nitrogen guarantee of 40 per cent. *Uramon* is a similar product manufactured in the United States and sold with a guarantee of 42 per cent nitrogen.

Urea nitrogen is readily soluble in water and is present in the amide form. Such nitrogen is classified as nonproteid organic.

Fertilizer grade urea has been extensively used in the preparation of mixed fertilizer and for direct application. Its high nitrogen content makes it especially well suited for use in the preparation of double strength and other high analysis fertilizers.

An informative discussion of the production and agricultural use of urea is given by Merz and Brown.[12]

Miscellaneous Materials. Ammonium chloride, bone meal, cocoa shell meal, cocoa tankage, diammonium phosphate, guano (bat), guano (Peruvian), leunaphos, leuna-saltpeter, linseed meal, mowrah meal, peanut meal, peat, phosphazote, potazote, rapeseed meal, soybean meal, tung meal, and urea-formaldehyde compounds have been used as nitrogenous fertilizers, but they are not commercially important at present.

BIBLIOGRAPHY

1. Andrews, W. B., Edwards, F. E., and Hammons, J. G., *Miss. Farm Research* **10**: No. 6, 3 (1947).
2. Bear, Firman E., "Soils and Fertilizers." New York, John Wiley and Sons, Inc. (1942).
3. Blair, A. W., *N. J. Agr. Expt. Sta. Bull.* **651** (1938).
4. Clark, K. G., and Bear, Firman E., *Am. Fertilizer* **108**: 7, 24, 26, 28, 30 (1948).
5. Clark, K. G., and Sherman, Mildred S., *U. S. Dept. Agr. Misc. Pub.* **593** (1946).
6. Collings, Gilbeart H., "Commercial Fertilizers." 4th ed. Philadelphia, P. Blakiston's Son and Co., Inc. (1947).
7. Jackson, M. L., and Chang, S. C., *Am. Soc. Agron.* **39**: 623 (1947).
8. Keenen, Frank G., *Ind. Eng. Chem.* **22**: 1378 (1930).
9. Lipman, Jacob G., in collaboration with Conybeare, Adrienne B., *N. J. Agr. Expt. Sta. Bull.* **607** (1936).
10. Mehring, A. L., *Ind. Eng. Chem.* **37**: 289 (1945).
11. Merz, Albert R., *U. S. Dept. Agr. Circ.* **185** (rev.) (1940).
12. Merz, Albert R., and Brown, Bailey E., *U. S. Dept. Agr. Circ.* **679** (1943).
13. Merz, Albert R., and Fletcher, C. C., *U. S. Dept. Agr. Circ.* **436** (1937).
14. Miller, E. C., "Plant Physiology." McGraw-Hill Book Co., Inc. 2nd ed., pp. 644–53 (1938).
15. Moore, H. C., "Am. Fertilizer Handbook." Philadelphia, Pa., Ware Bros. Co., pp. 21–57 (1946).
16. Parker, F. W., *Am. Soc. Agron.* **38**: 283 (1946).
17. Parker, F. W., "Science in Farming." U. S. Dept. Agr. Yearbook of Agr., pp. 561–5 (1943–47).
18. Parker, Frank W., Adams, J. Richard, Clark, K. G., Jacobs, K. D., and Mehring, A. L., *U. S. Dept. Agr. Misc. Pub.* **586** (1945).
19. Pierre, W. H., *Ind. Eng. Chem. Anal. Ed.* **5**: 229 (1933).
20. Pierre, W. H., *J. Assoc. Official Agr. Chem.* **17**: 101 (1934).
21. Pierre, W. H., *Com. Fertilizer Yearbook*, pp. 51–6 (1934).
22. Ross, W. H., Adams, J. Richard, Yee, J. Y., and Whittaker, Colin W., *Ind. Eng. Chem.* **36**: 1088 (1944).
23. Salter, Robert M., and Schollenberger, C. J., "Soils and Men." U. S. Dept. Agr. Yearbook of Agriculture, pp. 445–61 (1938).
24. Shreiner, Oswald, Merz, Albert R., and Brown, B. E., "Soils and Men." U. S. Dept. Agr. Yearbook of Agriculture, pp. 487–521 (1938).
25. Tiedjens, Victor A., *Plant Physiol.* **9**: 31 (1934).
26. Tiedjens, Victor A., and Robbins, W. R., *N. J. Agr. Expt. Sta. Bull.* **526** (1931).
27. Whittaker, C. W., and Mehring, A. L., *Fert. Rev.* **18**: No. 4, 1 (1943).

Chapter VIII

POTASSIUM FERTILIZERS

J. D. Romaine

American Potash Institute, Inc., Washington, D. C.

Potash fertilizers are used to supply plants with potassium, one of the elements essential for plant growth. Potassium is a soft, silvery-white metal that reacts violently with water. On exposure to air, it rapidly oxidizes to K_2O, which in the presence of water reacts to form the highly caustic KOH. For these reasons potassium in the elemental form cannot be used as a fertilizer, but must be combined with one or more other elements to form soluble compounds that will not damage plants when used under ordinary conditions. The chloride, sulfate, and nitrate compounds of potassium are the most common potash salts used as fertilizer.

There are five isotopes of potassium, K^{38}, K^{39}, K^{40}, K^{41}, and K^{42}. K^{39} and K^{41} are stable, K^{40} is naturally weakly radioactive with a half life of 10^9 years, while K^{38} and K^{42} can be rendered radioactive by artificial means, the half life of K^{38} being 7.7 minutes and of K^{42}, 12.4 hours.[12, 23, 31, 65]

The abundance ratios of these isotopes in naturally occurring potassium has not yet been fully worked out. K^{39} comprises over 93 per cent, K^{41} about 6.5 per cent, K^{40} around 0.01 per cent, whereas K^{38} and K^{42} are presumably still less abundant in normal K. Brewer [12] indicates plants may selectively absorb certain isotopes while Eckstein [23] does not believe so.

Throughout the world, the potassium content of fertilizer compounds is calculated to K_2O. This is called potash in the fertilizer industry, which uses the term rather loosely also in a generic sense for, and frequently synonomously with potassium. To convert K to K_2O, multiply by 1.2; to convert K_2O to K, multiply by 0.83.

For practical purposes it may be considered that the plant obtains all its potassium through the roots in the soil. When the natural soil supply cannot furnish sufficient potassium to meet the requirements of the plant growing on it, potassium must be added to the soil either in the form of fertilizer or manure if satisfactory growth of the plant is to be obtained.

Function of Potassium in the Plant

It is not known just what potassium does in the plant. Since practically all of it in the plant can be removed by washing, it is assumed that it does not enter into any of the component parts of the plant. Miller [56] points out that the only way it is possible to judge what it does is to observe how the plant reacts when it is supplied an insufficient amount for its normal physiological processes. Potassium is an active ion, easily absorbed by the roots and very mobile in the plant. The necessity of determining its role by more or less indirect means coupled with its mobility and activity have led to some confusion and contradictions in ascribing to potassium specific functions. Most investigators are agreed on a number of functions, but numerous other activities may be reported by one investigator and not confirmed by others. The situation is well expressed by Hoffer:[40]

> "Up to the present time, even though many physiological studies have been made on this element, there seems to exist little definite evidence indicating the nature of the mechanism by which potassium functions. It has a specific role in influencing the absorption of certain other mineral elements, in assimilating carbon, in translocating sugars and forming starch, in regulating the rate of respiration, in affecting the rate of transpiration, and also in influencing the action of enzymes. Many researches on these subjects show that potassium is necessary in all protoplasmic activity, but the chief difficulty is to allocate the exact function of potassium to specific steps in the whole series of these interrelated physiological processes. A disturbance in any one affects the whole series, and thus it is difficult to limit the interpretation of the results of research on potassium to any one physiological action in the plant."

Among the functions ascribed to potassium are that it is necessary for the formation of carbohydrates and their transference to the storage organs of plants.[40, 56, 78] In this same connection, it is involved in the assimilation of carbon dioxide.[59] The production of proteins is influenced by, although apparently is not dependent on it.[59] Potassium increases the stiffness of straw or stems due in part at least to increased thickness of the cell walls of the parenchyma.[25] Disease resistance is increased, due probably to a combination of effects such as increasing the vigor of the plant, increasing thickness of cell walls, changing the reaction of the cell sap, or influencing water relationships within the plant.

Cell division does not take place normally if potassium is not present, resulting in characteristic abnormalities of growth. This and many other of the activities of potassium may be due to the catalytic action of the element in plant metabolism. Jacob quotes Russell[42] as believing that potassium might compensate for reduced sunlight, based on observations of better response to potash fertilizers in years of low sunlight intensity. This has not been fully confirmed by other work. Since one of the isotopes of potassium is naturally radioactive, the only nutrient falling into this category, it has been suggested that the emitted rays might be utilized by the plant.[40, 42]

Potassium influences the absorption or activity of other elements in the plant, and in this way indirectly influences many phases of plant metabolism. By facilitating the movement of iron in the plant, potassium indirectly favors chlorophyll formation.[62]

Under certain conditions at least, potassium affects pigment formation, a matter of importance in fruit production. This may be a matter of biological balance with other elements, since this effect is not observed under all conditions. Potassium also seems to affect the moisture relationships within the plant, one well supplied with the nutrient being better able to withstand drought.

Since potassium is needed in the process of cell division, under conditions of insufficient supply, the plant tends to mobilize the limited amount present at the growing points at the expense of other portions of the plant. This may result in elongated rather than lateral growth. Under such conditions, the roots of sweet potatoes, beets, carrots, radishes, and similar crops will be long and "stringy," potato tubers long and narrow, and cucumbers constricted at the stem end. Further illustrations of the effects of potassium deficiency on plants will be found in the references.[24, 32]

When potassium is deficient more or less characteristic abnormalities frequently develop, among the most common being:

1. Necrosis along the edges of leaves, particularly noticeable on the broad-leaved plants and as firing on the edges of corn leaves.
2. Lodging of corn and small grains due to root rots and weak stalks or stems.
3. White spotting beginning along the edges of alfalfa, sweet clover, white clover, and other clover leaves.
4. Chaffy ears of corn, not well filled out to the tip of the cob.
5. "Rust" on cotton leaves, a bronze discoloration followed by necrosis and abscission of leaves causing poorly developed bolls that do not open well at maturity.
6. Potassium affects many of the factors in plant metabolism that in one way or another influence the harvested portion. In this way, the element is said to affect the quality of the crop.[7] It has been shown to have a favorable influence on the test weight of grains; the burn, fermenting and other characteristics of tobacco; the sugar content of beets and numerous other plants; and on the starch content of potatoes. For these reasons, potassium is frequently termed the "quality" element in plant nutrition.

Soil Potassium Supplies

Potassium occurs naturally in most soils as a constituent of feldspar and mica minerals, and their secondary derivatives.[48] The quantity of potassium that may be present in this form is deceptively large, in clayey soils possibly as high as 40,000 pounds K_2O per acre six inches.[20, 37, 55] The soil minerals as they slowly decompose will liberate some of the potassium in a form available to plants, but this quantity is frequently insufficient to furnish the amount required for intensive agricultural production.[4, 51] Sandy soils usually contain less of the potash-containing minerals, and peat and muck soils, none, so these soils have even higher potash requirements.

Although some potash usually is present in the soil solution, the potash that is available to plants is largely in a form that can be replaced in the soil minerals by hydrogen or other cations, and is therefore called the replaceable potash.[11, 44, 60] Nearly all methods for determining the available potash content of soils are based on the release of the easily replaceable potash. This is not an absolute guide to the amount of potash the soil can furnish a crop growing on it, since under some conditions more or less than this amount seems to be available to the plant.[4, 44]

Plowing under organic matter to induce the formation of organic acids which will react on the soil minerals to hasten their decomposition and consequent release of potash for plant use is one way of trying to utilize this large store of potash in the soil. Indeed, Hopkins[41] advocated this as a system of permanent agriculture for the midwest, but it is now generally agreed that, while this is to some extent effective, it is not sufficient to maintain high production on most soils.

POTASH LOSSES FROM THE SOIL

Potash is lost from the soil by crop removal, leaching, and erosion. These processes are continuous to a greater or less degree, depending on soil, climate, and farm management practices. Estimations of the losses of potash and other nutrients from the soils of the United States was made by Lipman and Conybeare.[47] Table 68 gives the data calculated to K_2O for harvested areas for the year 1930, and also the estimated potash returned to the land in one form or another.

TABLE 68. NET LOSSES OF PLANT NUTRIENTS FROM THE SOILS OF THE UNITED STATES

	Acreage	Tons K_2O
By harvested crops, 1930	367,554,485	3,824,149
By grazing	464,154,524	11,355,534
By erosion	367,554,486	34,990,589
By leaching	352,380,258	9,960,000
Total losses		60,130,272
Additions by fertilizers, manures, irrigation, etc.		6,181,291
Net annual loss		53,948,981

Table 69. Nutrient Content of Crops

Crop	Yield	Part of Crop	N lb.	P_2O_5 lb.	K_2O lb.	Total
Cotton	500 lb. 1,000 lb.	lint seed	38	18	14	70
	1,500 lb.	burrs, leaves, stalks	27	7	36	70
		Total	**65**	**25**	**50**	**140**
Tobacco	1,500 lb.	leaves	55	10	80	145
		stalks	25	10	35	70
		Total	**80**	**20**	**115**	**215**
Corn	60 bu.	grain	57	23	15	95
	2 tons	stover	38	12	55	105
		Total	**95**	**35**	**70**	**200**
Wheat	30 bu.	grain	35	16	9	60
	1.25 tons	straw	15	4	21	40
		Total	**50**	**20**	**30**	**100**
Oats	50 bu.	grain	35	15	10	60
	1.25 tons	straw	15	5	35	55
		Total	**50**	**20**	**45**	**115**
Barley	40 bu.	grain	35	15	10	60.
	1 ton	straw	15	5	30	50
		Total	**50**	**20**	**40**	**110**
Potatoes	300 bu.	tubers	65	25	115	205
		tops	60	10	55	125
		Total	**125**	**35**	**170**	**330**
Sweet Potatoes	300 bu.	roots	45	15	75	135
		vines	30	5	40	75
		Total	**75**	**20**	**115**	**210**
Sugar Beets	15 tons	roots	55	22	53	130
		tops	60	23	92	175
		Total	**115**	**45**	**145**	**305**
Tomatoes	10 tons	fruit	60	20	80	160
		vines	40	15	95	150
		Total	**100**	**35**	**175**	**310**
Cabbage	15 tons	all	100	25	100	225
Celery	350 crates	all	80	65	235	380
Spinach	9 tons or 1,000 bu.	all	90	30	45	165
Apples	400 bu.	fruit	20	7	30	57
		leaves, wood	10	3	5	18
		Total	**30**	**10**	**35**	**75**
Peaches	500 bu.	fruit	30	15	55	100
		leaves, wood	55	10	45	110
		Total	**85**	**25**	**100**	**210**
Grapes	4 tons	fruit	10	6	20	36
		leaves, canes	15	4	15	34
		Total	**25**	**10**	**35**	**70**
Oranges	600 boxes	fruit	65	23	105	193
		leaves, wood	25	7	25	57
		Total	**90**	**30**	**130**	**250**
Soy Beans	25 bu.	grain	110	35	40	185
	1.25 tons	straw	15	5	20	40
		Total	**125**	**40**	**60**	**225**
Peanuts	1 ton	nuts	60	10	10	80
	3 tons	vines	25	5	40	70
		Total	**85**	**15**	**50**	**150**
Pea Beans	30 bu.	grain	73	23	24	120
		straw	22	7	31	60
		Total	**95**	**30**	**55**	**180**
Alfalfa	3 tons	all	140	35	135	310
Sweet Clover	5 tons	all	185	45	165	395
Red Clover	2 tons	all	80	20	70	170
Lespedeza	3 tons	all	130	30	70	230
Cow Peas	2 tons	all	125	25	90	240
Timothy	1.5 tons	all	40	15	45	100

On this basis the net loss is enormous, and even today, allowing for reduced erosion and leaching and nearly three times as much potash fertilizer usage as in 1930, the net loss would be millions of tons of potash.

Losses from Crop Removal. Potash is present in nearly all parts of the plant, but not in equal proportions. It tends to be greater in the vegetative parts and less in the reproductive portions of the plant. When the type of crop is such that the plant as a whole is removed, as in hay or forage crops, or many of the vegetables, the loss from the soil by crop removal is greater than if only the seed portions are removed, as in the small grains. Table 69 on crop removals illustrates this.[63]

Particular attention is called to the legumes and hay crops at the bottom of Table 69. These are given much attention as soil conserving crops, and rightly so when properly used. The figures show, however, that if these crops are removed from the soil, they are highly soil-depleting with respect to potash. When considering the losses of potash from a farm, the amounts that go off in animal products should not be overlooked. Thus in each thousand pounds of milk sold, there are 1.8 pounds of potash, and in each thousand pounds of beef cattle, 1.7 pounds K_2O. While these losses are smaller than occur in crops sold off the farm, in the aggregate they represent considerable loss, especially in view of the fact that formerly it was thought that livestock and dairy farming did not deplete the soil.

Leaching Losses. The loss of potash in leaching varies considerably with the kind of soil, climate, and cropping and soil management system.[79] Soils with a higher absorptive capacity, usually the heavier soils with a high colloid content, will have lower leaching loss than the lighter, sandy soils and organic soils of low absorptive capacity. This is one of the reasons for the high potash fertilizer requirements of sandy and peat soils.

It is usually considered that potash is intermediate in its loss by leaching, lower than nitrogen and calcium, about the same as magnesium, but higher than phosphorus losses. High rainfall favors the loss of potash by leaching, but this can be reduced by cropping the soils. At the lysimeter experiments at Cornell University the annual loss by leaching of potash from two rather heavy soils averaged 82 pounds K_2O per acre when bare, and 69 pounds where the soils had a rotation of crops on them.[48] The loss of potash by leaching was about the same as loss by crop removal in the latter case.

Erosion Losses. The loss of potash through erosion is highly variable, being dependent on the total amount of soil eroded and its potash content. Data given by Bennett [9] indicate that the loss of potash through the various forms of erosion is ten to fifteen times as much as that of phosphorus or nitrogen, about the same as calcium and about twice the loss of magnesium. On the basis of these data, over 34 million tons of potash are lost in this way from the soils of the United States each year. The loss is usually higher on heavy soils, since the potash-containing minerals are likely to be in the finer, more erodible portions. Bennett gives data that show the eroded dust was 26 per cent richer in potash than the virgin soil from which the dust probably came.

The amounts of potash removed under several conditions of water erosion are illustrated in data obtained by Miller and Krusekopf in Missouri:[57]

Average Pounds of Potash in Eroded Material Removed per Acre Annually Between May 1, 1926, and May 1, 1928

Treatment	*Pounds K_2O*
Plowed 4 in. fallowed	1494.66
Plowed 8 in. fallowed	1442.48
Continuous bluegrass	3.20
Continuous wheat	316.80
Rotation: corn, wheat, clover	256.63
Continuous corn	726.36

On the continuous corn area, the potash lost in erosion is equal to that in ten crops of corn 85 bushels each, while on the continuous wheat area, the loss was equal to the potash in nine crops of 25 bushels each. These data were obtained under conditions of only moderate slope, and losses would be higher with greater slopes. Outstanding is the low loss under continuous bluegrass, showing the importance of cover on the soil in preventing loss by erosion.

Potash Additions to the Soil

Potash is added to the soil in fertilizers, manures, some mulching materials, seeds, and as alluvial and aeolial deposits. Lipman and Conybeare estimated potash additions to the soils of the United States for 1930.[47] Their data calculated on a K_2O basis are as follows:

	Tons K_2O
Fertilizers	359,464
Manures	3,331,523
Rainfall (dust)	1,835,280
Irrigation	592,531
Seeds	62,492
Total	6,181,290

These data would probably be about the same for 1948, except that the figure for potash in fertilizers would be around 900,000 tons of K_2O.

It will be observed that only in the case of fertilizer potash is there a real addition to the soil. In other cases, the potash is merely transferred from one soil location to another. Usually in this transference there is some loss of potash, some of which may be recovered within a reasonable time, but most of the rest eventually finds its way to the ocean and thus is lost until a feasible method of recovering potash from sea water is developed.

Barnyard manure is the largest single source of potash added to the soil. It could be an even more important source if it were handled properly. Bear [8] (p. 212) shows that 80 to 90 per cent of the potash consumed in the food of animals is returned in the manure. Unfortunately, it usually is so poorly handled that less than half of the original value is recovered. Potash losses in improperly handled manure are particularly high since a large part of the potash is in the easily lost liquid portions.

Mulching materials such as straw, hay, or green plants applied to the soil carry potash if they have not been leached before they are applied.

Additions of potash by alluvial and aeolian deposits are not a desirable means of meeting potash requirements. It is the most flagrant form of robbing Paul to pay Peter, and moreover, frequently the crop growing on the soil is damaged considerably when the addition is made. In most cases the recipient is the victim of circumstances and has to get what solace he can out of the thought that he may obtain some future benefit out of the current damage.

It is clear that additions of potash to a soil on a farm may easily balance the losses if soil management is good, but for the country as a whole, the deficit of removals over additions is so great that it must be narrowed by prevention of the enormous losses due to erosion, and reduction of leaching losses by good crop and soil management. These practices combined with the proper handling of manure and mulches, and the efficient use of potash fertilizers can permit the large potash resources of the soil to be conserved for future generations.

SECONDARY EFFECTS OF POTASH FERTILIZERS

Potash fertilizers seem to have little secondary effects on the soil. Potassium chloride, the most common form of potash fertilizer and potassium sulfate, the second most popular form, are theoretically physiologically acid, in that the potassium is absorbed more than the accompanying ion. This has been investigated very thoroughly by Kappen [43] (p. 289) and by Jacob [42] (p. 100). In water culture, the two forms proved to be physiologically acid, but in field work no tendency for acidity to develop in the soil from the use of potash fertilizers could be detected. Potassium nitrate and carbonate are physiologically basic, while potassium phosphate seems to be about neutral in its effect.

The unrefined potash salts, called manure salts in the fertilizer trade, contain considerable quantities of sodium chloride as an impurity. It has been indicated that under some conditions, the sodium may be of benefit.[34, 52, 66] On heavy soils the use of large quantities of manure salts is usually avoided due to the undesirable peptizing action of sodium on the soil colloids.

A deficiency of magnesium in soils may be corrected by the use of sulfate of potash-magnesia. This is of importance where a quick-acting soluble form of magnesium is desired, as in citrus and other fruit and vegetable growing and where it is not desired to raise the pH of the soil by the use of dolomite, as in growing potatoes and tobacco.

The principal secondary effect of potash fertilizers has to do with the chloride ion in the commonly used muriate of potash, or in manure salts. Plants absorb chlorine in rather large quantities if it is present in the soil. It does not seem to be essential but frequently exerts a stimulative effect on the growth of the plant. In the case of tobacco, however, a high chlorine content of the leaf interferes with the burn and other desirable qualities. For this reason the use of chlorine-containing fertilizers is limited or avoided when growing this crop.[30] Recently the Maine Experiment Station has reported unfavorable effects of chlorine on potatoes when large applications of muriate of potash were used over a period of years.[64] Growers of pineapples and some specialty crops also prefer to use potash fertilizers with a low chlorine content.

On soils where there is a high chlorine content, it usually is considered desirable to avoid the use of potash fertilizers in the chloride form, so as not to add more chlorine to the soil, even though the added chlorine would be comparatively insignificant in proportion to the quantity already present.

Analyses of the different grades and sources of potash fertilizer materials have been compiled by Turrentine.[76] These show a wide range of constituents, especially in the raw or unrefined salts. Michels[54] mentions a long list of elements that have been found in one sample or another of potash salts. Most of these constituents are present in very small and highly variable amounts, giving little reason to believe they would have any effect on the soil or on crop growth.

Classification of Potash Fertilizer Materials

The principal divisions of potash fertilizers are the chloride and nonchloride forms, the latter being mostly the sulfates. Since the chloride forms are cheaper than the others, they generally are used except where no chlorine is desired in the fertilizer. The principal nonchloride forms are the sulfate of potash and sulfate of potash-magnesia. Potassium nitrate,

nitrate of soda-potash, potassium carbonate, tobacco waste, cotton hull ashes, and some other plant ashes are used when available. They are largely chlorine-free, and therefore are in demand by growers of specialty crops, who usually pay a premium price for these forms. Residues of sugar (Steffens waste) and from alcohol refining and distillation; flue dusts; seaweed; wool waste; silicates such as feldspars, greensand marl, Georgia shale, leucite, porphyry copper mine tailings; and alunite are minor sources of potash fertilizers.

The silicates and alunite having low water solubility may be used locally where heavy applications can economically be made. They may also serve as raw materials for processing into water-soluble compounds. The use of the by-product and minor sources is rather fully treated by Turrentine.[73]

Use of Potash Fertilizers

Potash in the form of wood ashes was used to some extent in early colonial times for fertilizer purposes. Following the pronouncement of Liebig's theory of the mineral nutrition of plants in 1840, more attention was given to fertilization, and when potash deposits in Germany began yielding fertilizer materials in 1859, the United States began importation of them. For several years this country was the principal customer, a position later assumed by Germany.

Agricultural potash consumption in the United States increased slowly during the latter part of the nineteenth century, first reaching 100,000 tons K_2O per year in 1904. By the outbreak of World War I, over 250,000 tons a year were being used. When imports were cut off by the war, consumption perforce dropped to the levels of emergency American production, about 50,000 tons K_2O a year or less during 1917–1920. Following the resumption of imports, consumption again resumed its increase reaching about 350,000 tons in 1930. The depression caused a drop to less than 200,000 tons in 1932, but the next year began a rapid rise which with supplies augmented from the newly developed domestic industry continued with only minor interruptions, passing 900,000 tons in 1948, and probably will approach a million tons K_2O in 1949, as shown in Figure 10.[67]

The early use of potash fertilizers was along the eastern seaboard and in the southeast, due to the facts that the soils there had been farmed longer than the other soils in the country, and that in many cases they contained less native potash than many of the midwest and lower Mississippi Valley soils. As the latter regions and the West Coast continued to be farmed, in many cases with little or no fertilizer or manure being used, the potash in even these naturally fertile soils became depleted. This gradual depletion was not given particular attention by most farmers, reductions in yield resulting therefrom being ascribed to such factors as unfavorable weather, plant diseases or pests, or seed lines "running out." Agricultural research and educational agencies on the basis of their longtime experiments and employing the modern techniques of soil and plant tissue testing and analysis realized the serious situation that was developing and urged farmers to give more attention to soil depletion. This, combined with the urge to produce at the maximum during World War II and plenty of money with which to purchase potash and other fertilizers, led to a rapid increase in demand, especially in the newer fertilizer-using portions of the country. Usage in the older eastern and southern parts of the country is more stable and has not increased proportionately as much as in the newer sections. The older sections still are using more tons of potash than the newer sections, but this position also is changing and the Midwest is beginning to challenge the South as the principal potash-using section of the country. Even in the drier sections of the country the use of irrigation is opening new areas to the use of potash fertilizers, and in 1947, some use is reported in every state of the country (see Figure 11). The same general trends hold for Canada.

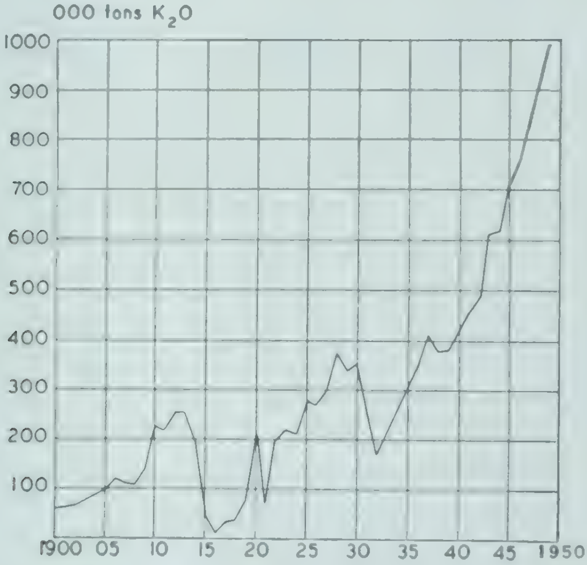

FIG. 10. Estimated potash consumption in the United States.

Except during World War I, potash prices have been rather steady and relatively low, so price has not been much of a factor in limiting its use and, under present price relationships, is highly favorable to its use. The producers' price of muriate of potash (60–62% K_2O) from 1937 to 1947 was 53.5 cents a unit (a unit is 1 per cent of a short ton, or 20 pounds) K_2O, at Atlantic and Gulf ports, with a seasonal discount of 12 per cent under which most of the potash is sold, bringing the net price to 47.1 cents a unit. During most of this time it was possible also to purchase this potash f.o.b. Carlsbad, New Mexico, at a differential of 11.2 cents a unit, or 42.3 cents list and 35.9 cents a unit net. Beginning in 1947, the producers quoted only f.o.b. Carlsbad, and reduced the price to 37.5 cents a unit list and 33.0 cents under the seasonal discount for muriate of potash. Turrentine [74] and Backman [5] give further information on prices.

The relative use of the different forms of potash fertilizers has been considerably influenced by price. When most of the potash came from Europe, the cheapest form along the Atlantic and Gulf coasts was for a time manure salts, and large quantities were used. As potash usage developed farther inland and freight costs were added to the port price, a demand for higher analysis materials resulted in muriate of potash containing 50 to 62 per cent potash becoming the most popular carrier. The American industry being located long distances from the important consuming sections, there was still greater impetus given to the development of concentrated materials, so that today the principal grade of potash fertilizer is the 62 per cent K_2O muriate of potash, which runs about 99 per cent KCl. The sulfate forms of potash, being manufactured products for the most part, have always been more expensive and this limits their use to special conditions where a low chlorine content of the fertilizer is desired. The consumption of various forms of potash fertilizers is shown in Table 70.

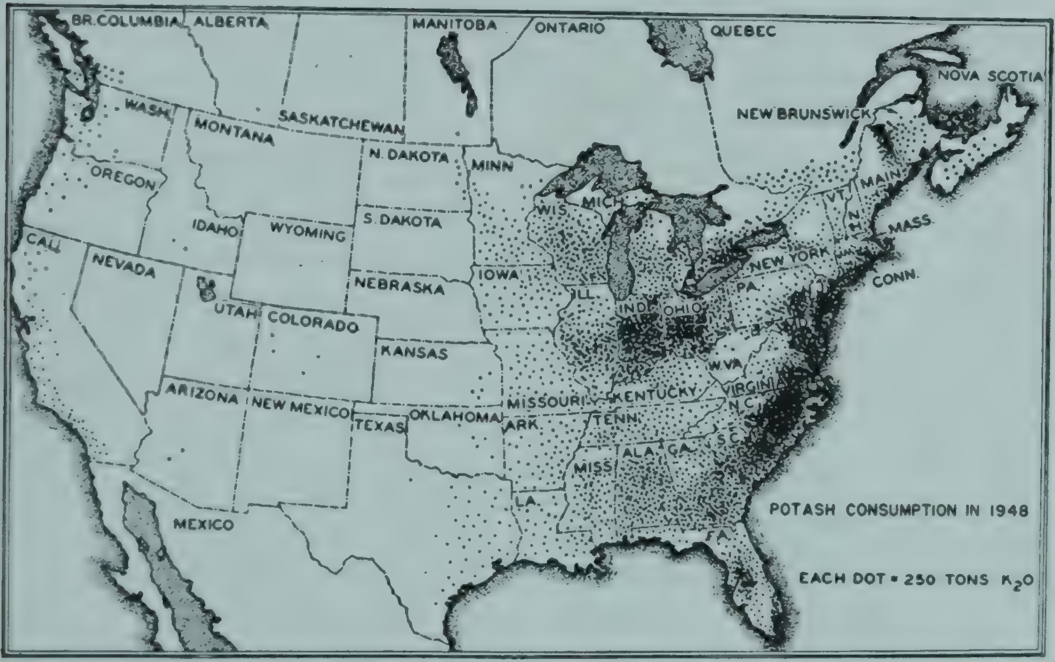
BR. COLUMBIA
ALBERTA
MANITOBA
ONTARIO
QUEBEC
NOVA SCOTIA
NEW BRUNSWICK
SASKATCHEWAN
WASH.
MONTANA
N. DAKOTA
MINN
OREGON
MAINE
VT.
N.H.
MASS.
WIS.
MICH.
S. DAKOTA
IDAHO
WYOMING
CALIF.
NEVADA
NEW YORK
CONN.
IOWA
NEBRASKA
PA.
ILL.
IND.
OHIO
UTAH
COLORADO
KANSAS
W.VA.
MISSOURI
KENTUCKY
VIRGINIA
N.C.
ARIZONA
NEW MEXICO
OKLAHOMA
ARK.
TENN.
TEXAS
S.C.
MISS.
ALA.
GA.
LA.
FLA.
MEXICO
POTASH CONSUMPTION IN 1948
EACH DOT = 250 TONS K_2O

FIG. 11. Potash consumption in 1948.

For many years cotton led all other crops in the consumption of potash, but in recent years, the increased use of potash on corn in the Midwest as well as in the South has put this crop in first place as a potash user, followed by fruits and vegetables as a group, cotton, potatoes, wheat, and tobacco.

Under normal conditions, about 90 per cent of the potash is used by farmers as an ingredient of mixed fertilizers, the other 10 per cent being used either alone mostly as a top dresser material or purchased by the farmer as a material to be mixed with other materials prior to application.

TABLE 70. POTASH DELIVERIES IN NORTH AMERICA BY GRADES—SHORT TONS K_2O *

Year	60% Muriate tons K_2O	50% Muriate tons K_2O	Manure Salts tons K_2O	Sulphates tons K_2O	Chemical Grades tons K_2O	Totals tons K_2O
1936	227,520	78,725	32,314	38,291	18,174	395,024
1937	293,144	119,975	37,528	47,914	17,997	516,558
1938	267,130	120,659	25,972	44,879	15,585	474,225
1939	245,009	78,578	11,262	30,206	24,284	389,339
1940	315,366	82,139	12,131	34,442	38,028	482,106
1941	348,523	45,002	32,560	34,231	51,962	512,278
1942	458,613	42,518	48,286	46,987	63,844	660,248
1943	489,413	51,152	53,819	51,610	84,367	730,361
1944	561,663	52,614	51,244	57,727	83,120	806,367
1945	620,300	64,564	37,031	60,433	85,858	868,186
1946	689,248	63,980	22,561	73,017	76,137	924,943
1947	813,139	69,445	46,272	79,464	82,707	1,091,024
1948	859,342	73,692	68,439	84,343	88,226	1,173,842

* Data include imports of European potash prior to 1942 and since 1946 French and German imports of non-Russian origin.

In those sections where rock phosphate is used by farmers, there is a demand for potash materials for direct application alone to the crop to supplement the rock phosphate which can be applied in larger quantities and less frequently than can the more soluble potash fertilizers.

PRODUCTION OF POTASH FERTILIZERS

The production of potash fertilizers is confined largely to Germany, France, United States, Spain, Russia, Israel, and Chile. Small amounts are produced in other countries but they have little significance in world commerce.

Germany. The production of potash for fertilizer purposes followed shortly after the discovery of potash in the salt deposits at Stassfurt, Germany, in 1851. Salt springs in this area had long been known and borings were begun in 1839 [46] to determine the extent of the suspected salt deposit, with the objective of developing table salt production. In 1851 the operation was halted due to the presence of potash and magnesium salts in the borings giving the rock salt such an unpleasant taste as to make it unsuitable for human use. In spite of this disappointing development, two shafts were begun the latter part of the year. These shafts reached 255.5 meters depth in 1856 where rock salt with potash and magnesium impurities was encountered. These impurities were separated by hand from the desired rock salt and discarded, for which reason they were called "Abraumsalze," or waste salts, an appellation that persisted for some years. The raw salts were also called "Stassfurtersalze." There was immediately some interest in the use of them as fertilizer, but results were not always satisfactory since they were for the most part the mineral carnallite, consisting of KCl and $MgCl_2$, the latter having an unfavorable effect on plants if present in large quantities.

In 1861 a factory for the separation and purification of the potassium, magnesium, and other salts in the carnallite was begun, which Krische [46] calls the beginning of the chemical potash industry. Small amounts of the purified KCl were used as fertilizer but the principal outlet was for the preparation of potassium nitrate and other potassium compounds. The discovery of kainite in a neighboring mine in 1865 opened the way for the development of a potash fertilizer industry, since this mineral, consisting of potassium chloride and magnesium sulfate, was free of magnesium chloride. Kainite gave good results when used as a fertilizer, and rapidly became popular in Europe and America. Industrial uses, however, continued to be the principal outlet for the potash production until 1890, when agricultural use forged ahead, and rapidly assumed its present predominant position in the potash industry.

Up to the end of World War I, Germany, with practically a world monopoly on the known potash deposits, had to meet the world's increasing potash fertilizer requirements. This led to a rapid increase in potash production in the country, at one time 209 mines being in operation. Overproduction resulted and later output was consolidated in some 45 of the most efficient mines and refineries.

The German potash deposits are the world's largest easily workable ones, so far as is definitely known. The principal minerals being worked are carnallite (mainly KCl, $MgCl_2$, and NaCl), Hartsalz (KCl, NaCl, and $MgSO_4$) and sylvinite (NaCl and KCl). The formerly important kainite (KCl and $MgSO_4$ with NaCl as impurity) is no longer being mined. The strata containing this mineral are nearest the surface, with consequent greater danger of water breaking into the mine. After several disasters of this nature, practically all production of kainite was stopped, although the name was retained for trade purposes to apply to run-of-mine salts containing 14 to 20 per cent K_2O for fertilizer purposes.

Geologically, the deposits are of Permian origin but have been subjected to later folding and other actions resulting in irregularity to a greater or less degree in the strata. Most of the mines operate at depths of 1100 to 2800 feet, the deepest being 3600 feet.[42, 61] The veins are 8 to 30 feet or more in thickness, the average K_2O content being 8–18 per cent.

France. Potash deposits were identified in Alsace in 1904, when prospecting for oil or coal, although the presence of underground salt deposits had been known since 1869. A shaft was begun in 1907, and production commenced in 1910.[1, 21, 42, 61] Since at that time Alsace was a part of Germany, this did not affect the German monopoly on potash supplies. The Treaty of Versailles in 1918 awarded Alsace to France, thus breaking the German monopoly. The French developed the Alsatian mines more intensively than had the Germans and France soon became an important exporting country. In 1924 the German and French potash industries reached an agreement on world sales policies, whereby each country supplied its domestic needs out of its own production. A Dutch company was set up to handle promotion and sales in foreign countries, Germany to supply 70 per cent of the potash, and France 30 per cent. Later Spain and Poland joined in the organization and were given quotas of the world market.

The French deposits are of Tertiary origin and are not related geologically to the German deposits. The principal mineral is sylvinite, occurring in two beds at depths a little over 2000 feet. The upper bed averages 4 feet in thickness, and 20–22 per cent K_2O, while the lower bed is 8 to 10 feet thick, with 14 to 18 per cent K_2O.[61]

A second deposit of potash salts occurs in the southwestern part of France near Dax, in the Departments of Landes and Basses Pyrénées. This deposit contains several strata of sylvinite at depths around 2500 feet. In some places, kieserite also is found, the only known occurrence of this mineral in France. The potash content of the deposit averages around 12–17 per cent K_2O.[13]

This deposit apparently is of a different geological origin than the Spanish potash deposits to the south of the Pyrenees. Exploration indicates the salt beds to be less extensive than in Alsace, but they are being developed and a small but regular production is reported.

Galicia (Poland). The presence of potash in the salt deposits of Eastern Galicia was long known, and Krische quotes Majewski as claiming these to be the first potash salt deposits ever discovered.[46] Kainite was encountered when sinking a shaft for a salt mine in 1804 and later in other shafts, sylvinite was found. As in the case at Stassfurt, these salts were considered a liability, since table salt was the objective of the operations.

After Liebig propounded his theory of the mineral nutrition of plants in 1840, interest in the potash content of these salts developed, and by the middle of the nineteenth century, a yearly production of about 30,000 tons of sylvinite had been reached. In 1886, the Austrian government, to which Galicia then belonged, began a more intensive development of the kainite deposit, production reaching 18,000 tons in 1911, only a part of which apparently was used as fertilizer. During World War I, production practically ceased but was resumed by the Polish government following the reestablishment of this country and the inclusion of Galicia in it. Production mounted rather rapidly until World War II when it was reported the mines were severely damaged. Galicia now seems to have been taken over by the Russians, and it is presumed that the Polish potash industry there is now in Russian hands.

Recently there have been reports of the discovery and exploitation of new potash deposits in the Kujawy district of Poland, with output expected to begin in 1952 or 1953.

United States. Although the United States had an important potash industry in wood ashes during colonial times, the discovery of the Stassfurt deposits in Germany and the reduction of the native forests relegated the wood ash industry so much to the background as to make it a negligible factor.[16] Deposits of water-insoluble potash-containing minerals such as the greensands of New Jersey and feldspars, and partially dried-up lakes in the West were known and utilized locally but no industry built up around them as sources of potash.

Udden in 1912 found potash in brine of a well in the Permian Basin area of Texas, although no potash mineral was identified until 1921 when polyhalite was found near Midland, Texas.[69] With the cutting off of potash supplies from Germany at the beginning of World War I, an intensive search was made for possible sources of potash in this country. The partially dried up lakes in the West were the most apparent source of potash and the most quickly utilizable. Under the impetus of wartime requirements and prices ten times normal, a potash industry rapidly developed, 128 plants being established. Many were located at saline lakes in California, Nebraska, Nevada, and Utah. The output of these was supplemented by potash produced from kelp on the west coast, cement dust, blast furnace dust, Steffens waste, distillery waste, alunite, leucite, greensand marl, Georgia shale, wood ashes, plant ashes, and tobacco waste.[73, 75, 82]

Mildly alarmed by our dependence on foreign sources for potash, Congress in 1910 authorized an exploration into possible domestic sources of potash. With the cutting off of German potash in 1914, this search was intensified. The efforts were successful in locating potash to meet our most urgent requirements, a peak of 55,000 tons K_2O being produced in 1918.

With the resumption of European importations following the end of the war, prices dropped from their high wartime levels. The war-born industry could not continue under normal prices and the plants rapidly ceased operations. Only one, that of the company now known as the American Potash and Chemical Corporation on Searles Lake, California (see Figure 12) was able to survive, and even this only after a most thorough overhauling of its processes.[71] Here, a brine of complex composition is the raw material from which high-grade muriate of potash is obtained, with borax, salt cake, soda ash, and other compounds as by-products.[29] By reacting the KCl with the Na_2SO_4 under appropriate conditions, sulfate of potash also is produced.

FIG. 12. View of Searles Lake surface with Trona, Calif. in the background.

The brines of the Salduro Marsh in western Utah containing 1.5 to 3 per cent KCl were utilized as a source of potash during World War I but, in common with most other potash enterprises of that period, the operations were not able to survive under normal conditions.[73, 74] In 1938, after a lapse of twenty years, production was resumed by Bonneville, Ltd., with a plant near Wendover, Utah. Utilizing solar evaporation in the first stages and flotation methods for final refining, a high-grade muriate of potash is produced (see Figure 13). Output is much less than the New Mexico and California operations, but is an important factor in the fertilizer market.

Some of the by-product operations, such as recovery from cement dust and distillery waste, continued to produce small quantities of potash. Sulfate of potash is being obtained from cement dust at a plant in Maryland.

and a distillery in the same state until recently obtained a fertilizer grade of potassium carbonate from its wastes, but a shift in source of raw materials resulted in a termination of this production.

Further explorations for potash deposits in this country were authorized by Congress in 1926. The work was concentrated in a portion of the Permian salt basin in New Mexico, Texas, and Utah, as being similar in many respects to the geological formation in which the German deposits are found.[69] Considerable polyhalite, a mineral consisting of sulfates of calcium, magnesium, and potassium, and some sylvinite, a mixture of potassium and sodium chlorides, as well as other minerals were found in thicknesses and purities and at depths as to indicate commercial exploitation possibilities. In 1925, a private oil company drilling near Carlsbad, New Mexico, found potash in its drillings, later identified as sylvinite. This led to the establishment of what today is the United States Potash Company, which in 1931 began producing a highly refined muriate of potash and also run-of-mine salts, called manure salts, for fertilizer use.

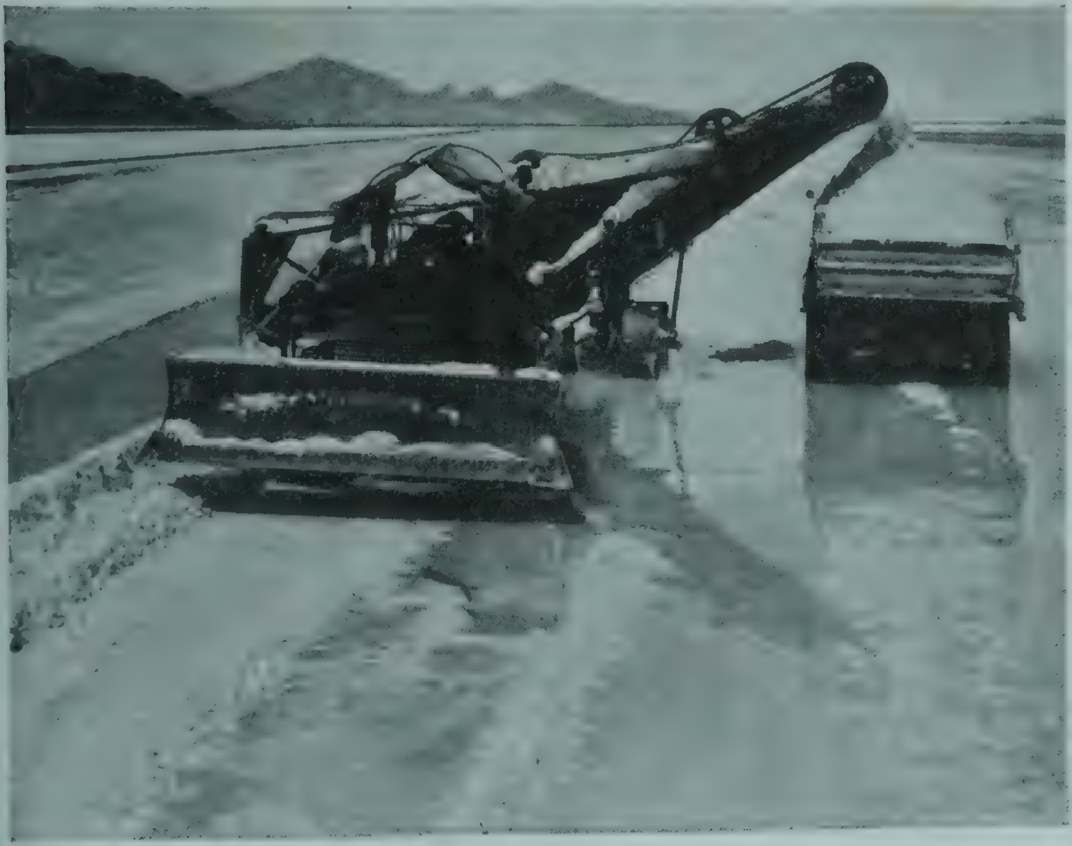

FIG. 13. Potash harvesting from salt flats by Bonneville, Limited near Wendover, Utah.

A second company, the Potash Company of America, began operations near-by in 1933, and production in 1934. In addition to muriate of potash and manure salts, this company later made arrangements with sulfuric acid plants in Tulsa, Oklahoma, and Dallas, Texas, and is now erecting a plant of its own at Dumas, Texas, to convert some of the KCl to K_2SO_4 to meet a need for this compound in American agriculture and industry.

The International Minerals and Chemical Corporation is a third company operating in this same area, beginning in 1936 as the Union Potash Company, itself a consolidation of several other potash companies. Production began in 1940. The deposits of this company, in addition to sylvinite, contain langbeinite, a mineral of potassium sulfate and magnesium sulfate. This company is therefore turning out sulfate of potash and also langbeinite for direct use as fertilizer, as well as muriate of potash and some manure salts. The Continental Potash Company has begun operations near Carlsbad, testing the Cross solution method of mining. No commercial production has yet been reported.

Some potash for fertilizer purposes is obtained from underground brines in Michigan, by the Dow Chemical Company. Small amounts of potash are shipped from time to time as alunite from Utah, shales from Georgia, greensand marl from New Jersey, and other very minor sources.

Plant and animal wastes are a source of potash for fertilizer use, and consist of such materials as tobacco stems, cotton hull ash, and wool waste. A total of some 15,000 to 20,000 tons K_2O is obtained yearly from these sources, according to estimates by Mehring.[53]

The American potash industry has made some remarkable records. It was born out of necessity during World War I and practically collapsed in 1921 when European imports reappeared on the American market. Since that date a new industry has been developed which has increased production steadily with only minor interruptions until in 1950 about 1,255,000 tons K_2O were produced. An even higher figure would have been reached in 1950 if a strike of potash miners in the important Carlsbad producing area had not shut down most of the operations in January of the year. The present American potash industry probably could produce nearly 1.5 million tons K_2O a year if called upon to do so. Explorations and plans of two additional companies in the Carlsbad area indicate that additional production will be available within several years. At the outbreak of World War II, the American potash industry was supplying about half the American requirements, but immediately began a series of expansions which have enabled it to meet substantially all the North American agricultural and industrial requirements (see Figure 14). In marked contrast to most other industries, the prices average about the same as prewar. This was accomplished without any government subsidy, financial assistance, or tariff protection.

Spain. Potash deposits were discovered in Spain in 1912 and were exploited by Spanish and foreign interests until an important industry was built up.[70, 74] The deposits are at easily workable depths and consist mostly of carnallite and sylvinite. Most of the production is refined to muriate of potash and considerable quantities are exported.

Russia. Deposits of slyvinite were found in the Province of Perm, in the Ural mountains of Russia in 1925. It is difficult to obtain exact data on the Russian industry, but production of potash salts is reported to have begun in 1930 and increased rather rapidly. The Russians claim they have huge potash reserves in this deposit, even larger than those of Germany. They are developing these on a large scale, one mine and refinery reportedly being the largest in the world. Discovery of other potash deposits in various parts of Russia are mentioned in the technical press, but little definite information concerning them is available. It would appear as if Russia has the potentialities of becoming the largest potash producer and even before World War II was exporting some potash to the United States and other countries. Indications of increased requirements for its own agriculture may limit Russian exports.

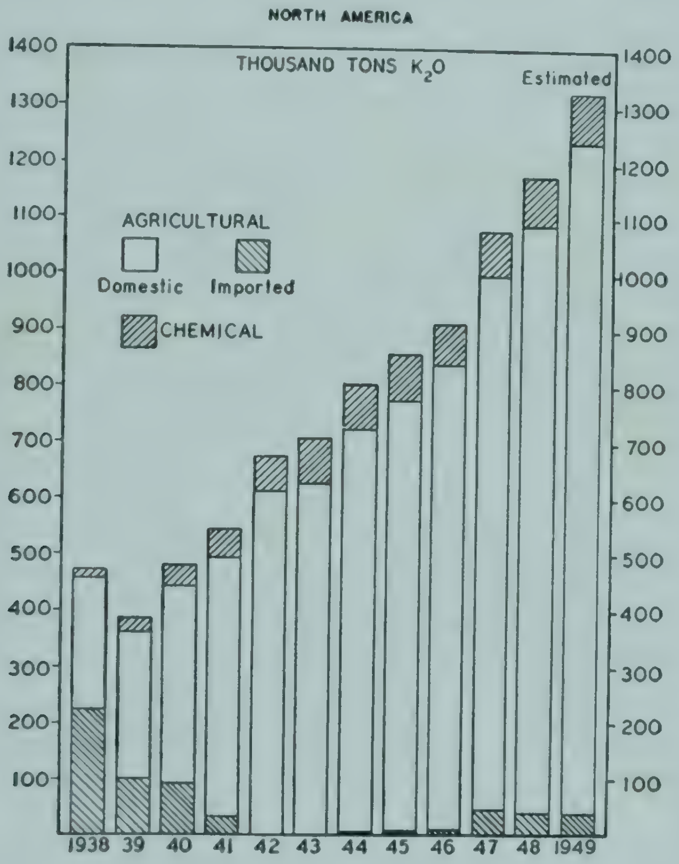

FIG. 14. Potash deliveries—agricultural and chemical—North America.

Palestine and Israel. The recovery of potassium chloride and other chemicals contained in the waters of the Dead Sea was begun in 1930. Using solar evaporation methods, concentrated muriate of potash is prepared for use domestically and export as fertilizer. Production increased steadily, reaching a high of 52,500 tons K_2O in 1944, but has dropped off during the last several years due to internal strife in the country.

Chile. Some of the Chilean nitrate of soda deposits contain small amounts of potassium nitrate that can be recovered in the refining process as a mixture of sodium and potassium nitrates or as straight potassium nitrate. These have found ready use as fertilizers. They usually are classified as nitrogen materials, both containing about 15 per cent nitrogen, with the potash content 15 and 44 per cent, respectively.

Italy. In contrast to the water-soluble potash deposits that are worked in most countries, those of Italy are not soluble in water. They consist of the mineral alunite, a hydrated potassium aluminum sulfate, and leucite, a potassium aluminum silicate. The alunite deposits are stated by Turrentine to contain about 200,000 metric tons K_2O, while the leucite is much more extensive, containing an estimated 8 billion tons or more K_2O.[74] Although some effort has been made to develop both these deposits, the leucite has received more attention. The treatment of the alunite usually involves heating to high temperature, addition of a neutral salt such as sodium carbonate, extraction, and crystallization. Leucite usually is treated with an acid to dissolve out the potassium and aluminum, followed by the separation and precipitation of the two salts. In both processes, alumina as a by-product is needed to help carry the costs. While these sources of potash appear to be sufficiently promising to attract governmental and private investment on a limited scale, technological difficulties and costs of production apparently prevent the development of a large industry.

Other Countries. Potassium nitrate deposits in limited amounts occur in India and a number of other countries. These are worked from time to time and the product appears on the market occasionally for fertilizer use.

Reports of an extensive sylvinite deposit in southern Saskatchewan, Canada, have recently appeared.[15, 80] The limited amount of exploratory work to date indicates a substantial body of salt, but at depths of over 3000 feet. While this is about three times as deep as the New Mexico deposits, it is no deeper than some of the German mines, indicating possibilities of commercial exploitation. The deposit extends to the north for several hundred miles, apparently at decreasing depths, but the thickness and extent of the potash strata are not yet known.

Potash is produced from kelp on a limited scale in Japan, and deposits have been reported at one time or another in many countries, among them Abyssinia, Austria, Brazil, Denmark, England, Iran, Korea, Mexico, Peru, and Sweden. Statements on processes for the recovery of potassium in sea water are occasionally heard. It was reported that during World War II such a process was put in operation in Norway. This is possibly a process said to use dipicrylamine as the precipitating agent, which can be recycled. A factory has been built near Saldanha Bay in South Africa for the purpose of extracting potash and other products from sea water. No mention is made of the processes to be used.[2]

TABLE 71. POTASH PRODUCTION BY PRINCIPAL COUNTRIES *—SHORT TONS K_2O FOR UNITED STATES, METRIC TONS K_2O FOR ALL OTHER COUNTRIES

Year	Germany	France	Poland	Spain	Russia	Palestine and Israel	United States
1915	740,000						1,090
1916	940,000						9,720
1917	970,000						32,573
1918	1,010,000						54,803
1919	850,000	96,546	254				32,474
1920	1,296,929	194,355	1,030				48,077
1921	933,400	144,836	1,568				10,171
1922	1,301,900	211,674	15,479				11,714
1923	1,059,700	262,404	29,404				20,215
1924	895,600	271,625	17,981				22,903
1925	1,574,839	311,892	37,597	2,640			25,448
1926	1,182,589	366,670	38,942	6,016			23,366
1927	1,518,037	370,901	43,825	16,216			43,510
1928	1,691,128	406,640	55,611	22,557			59,910
1929	1,787,775	492,097	63,735	22,602			63,735
1930	1,608,514	506,370	55,230	28,039	5,000	1,200	61,270
1931	1,077,632	367,879	52,741	28,116	?	2,600	63,880
1932	871,354	326,500	57,044	54,811	?	5,100	61,990
1933	1,026,000	332,000	77,370	91,113	42,122	7,500	143,378
1934	1,329,000	356,100	61,978	131,648	200,500	8,982	144,342
1935	1,596,972	342,270	73,209	120,396	260,000	9,600	192,793
1936	1,622,650	368,880	83,915	49,365	225,000	11,727	247,340
1937	1,968,416	489,801	99,940		266,000	18,234	284,497
1938	1,861,000	581,790	108,352	15,120	122,000	29,059	316,951
1939	1,750,200	598,000		25,526	?	31,764	312,201
1940	1,745,900	517,000		89,653	?	45,000	379,679
1941	1,824,300	673,000		101,039	?	50,840	524,875
1942	1,744,700	619,000		89,654	?	52,100	679,206
1943	1,746,900	664,497		87,380	?	46,900	739,141
1944	1,604,500	466,657		115,830	?	52,500	834,568
1945	850,000	144,701		113,700	?	46,800	874,243
1946	605,000	534,495		135,479	280,000	45,300	931,812
1947	900,000	711,200		153,652	500,000	61,600	1,029,875
1948	1,140,000	769,000		152,000	?	?	1,139,881
1949	1,500,000	879,000		?	?		1,150,000

* All 1949 figures are preliminary, as are also 1948 figures except for United States.

Alunite deposits at Lake Campion, Australia, are being worked. Output is about 30 tons K_2O a week, with plans under way for expansion to a production of 20 tons a day.[3]

A summary of the potash production of the most important areas of the world is given in Table 71.

MINING OF POTASH SALTS

In the mining of potash salts, two shafts usually are sunk to or through the potash-bearing strata. One shaft is used for the hoisting equipment and air intake (shown in Figure 15). The second shaft usually is smaller and is used as an escape for emergency purposes and as an air outlet in ventilating the mine. The salts are removed by the room and pillar method, about 60 per cent of the ore body being removed with 40 per cent left in pillars which are the sole support needed in the mine. It is stated by McGraw that when a mine is worked to the end of the deposit or to such a distance from the shaft as to make it too expensive to haul the ore to the shaft, the pillars can be systematically robbed. The 600 feet of salt overburden is believed to be sufficiently elastic to permit it to bend to the floor instead of breaking.[19] Dolbear estimates that another 20 per cent of the deposit can be recovered in this way.[22]

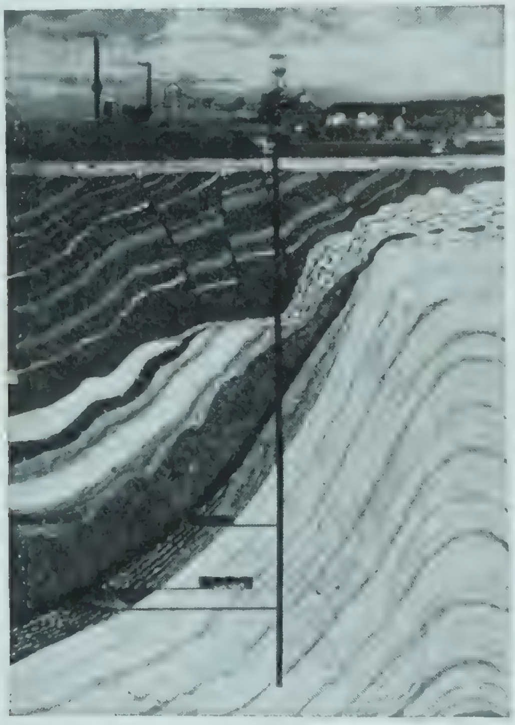

FIG. 15. Cross section of a European mine. The principal potash salts are in the dark, streaked layer next to the bottom. The bottom or thick white deposit is rock salt.

The potash layer is undercut at its lower boundary and blasted loose. The broken ore is loaded by dragline or mobile loaders into mine cars which are taken to a dump near the hoisting shaft. In some mines the potash is crushed at the bottom of the shaft before hoisting. In others it is crushed after being brought to the surface, where most of it goes to the refinery for processing, while some is shipped for direct use as fertilizer. The work in the potash mines is highly mechanized. Water must be rigidly excluded with the result that the mines are clean and dry.

POTASH RESERVES

The total amount of potash in the world is very large. Hilgard[37] quotes Clarke and Washington as estimating that the earth's crust contains about 3 per cent potash. Much of this is of no use from the fertilizer viewpoint, as it may be too deep to be used, too insoluble to be utilized by plants, too dilute to be transported to areas where needed, or too difficultly transformed for fertilizer use. While potash is thus very widespread in nature, the concentrated deposits that are easily workable are comparatively few in number, although some of them are great in extent.

Germany has always been considered to possess the greatest reserves of easily workable potash salts. Recent data from Russia give much larger figures for that country, which if authenticated would place its reserves at several times the known reserves of the rest of the world put together. Turrentine compiled data on known reserves as follows[74] (p. 49):

Estimated World Potash Reserves
(Million tons K_2O)

United States	85
Russia	700
Poland (Galicia)	10
Germany	2500
France	300
Spain	270
Palestine	1200

A thorough appraisal of the known potash reserves in the United States was recently made by Dolbear.[22] He shows over 100 million tons K_2O in easily workable deposits in operation today. The large polyhalite deposits represent reserves nearly two and a half times as much, and the insoluble reserves are about eight times greater than the easily workable reserves. While these second and third categories probably could not be operated at the prevailing low prices for potash, present technological information indicates they could be used if the price were higher. They thus represent reserves of great magnitude that can be called on if they are needed.

POTASH FERTILIZER MATERIALS AND THEIR PRODUCTION

Muriate of Potash. This is by far the most important potash fertilizer, quantitatively, approximately 87 per cent of the total K_2O used in North America in 1947 coming from this source. It is the neutral salt potassium chloride, with sodium chloride the principal impurity. The color may be white, gray or red, the latter color being due to the presence of traces of iron. It comes on the market in grades ranging from 50 to 62 per cent K_2O, corresponding to 80 to 98 per cent pure KCl. In North America, the 60–62 per cent K_2O grade, corresponding to 95–98 per cent KCl, is the most popular, constituting 80 per cent of the agricultural potash used in recent years. The 50 per cent grade, corresponding to 80 per cent KCl, makes up about 7 per cent of the agricultural potash, although prior to 1935 this was the principal grade in North America, and still is in many parts of the world.

Potash-bearing salt minerals, usually subterranean, are the source material for most of the muriate of potash production. These may be the salt rocks sylvinite consisting of the minerals sylvite (KCl) and halite (NaCl); carnallite consisting mostly of the mineral carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$); and Hartsalz, a mixture of sylvite, halite, kieserite ($MgSO_4 \cdot H_2O$) and or anhydrite ($CaSO_4 \cdot 2H_2O$). All of these occur in the German and Russian deposits while in the United States nearly all muriate of potash production in the New Mexico area is from sylvinite, as is the largest part of the French and Spanish production. Brines serve as the source of raw material in some of the American operations and in Palestine.

Two types of refining processes are used to separate the potassium chloride from the other compounds that may be present. One type involves the separation of the KCl out of solution by crystallization. When brines serve as the raw material, this type of process must of necessity be employed in at least the first steps of refining while when starting with crude salts, they must first be put in solution. The second type of refining employs separation by physical means, based on flotation principles and differences in specific gravity of the potassium chloride and other crystals.

Crystallization Processes. In most of the raw materials from which potassium chloride is separated, the principal impurity is sodium chloride, with varying quantities of magnesium chloride and sulfate, calcium sulfate, and insoluble matter such as clay. The fundamental principles involved in refining are therefore the same in the various plants over the world, being based on the classical phase rule studies of van't Hoff. Details of the processes vary with the composition of the raw material used and modifications worked out in the several plants seeking to achieve the maximum efficiency in operation.

The raw salts are crushed and dissolved nearly to the saturation point in hot water or hot mother liquor already nearly saturated with respect to sodium chloride, thus eliminating the insoluble matter, which is largely clay, most of the gypsum and much of the sodium chloride. Advantage is then taken of the fact that potassium chloride is much more soluble in hot water than in cold, while the solubility of sodium chloride does not vary much with temperature of the solution.[18, 28, 54] On cooling the nearly saturated hot solution, the potassium chloride crystallizes out and the sodium chloride remains for the most part in solution. Since the magnesium salts are more soluble than the potassium salts, these also remain in solution.

In the older refineries in Germany, the cooling and crystallization were carried out in large iron vats (see Figure 16). The more modern refineries in European countries and all those in this country using crystallization methods, now employ vacuum cooling (Figure 17) for the crystallization of the potassium chloride. This is much more rapid and efficient than the older crystallization vats, and has been one of the most important improvements ever introduced into the potash industry.[28, 35, 54, 74] The solution remaining after the potassium chloride has been removed is largely recycled to serve as the mother liquor for dissolving new charges of raw salts. In some plants compounds of magnesium, sodium, bromine, boron, lithium, and other elements present in the raw material gradually build up in the mother liquor to the point where they can be economically removed as valuable by-products.

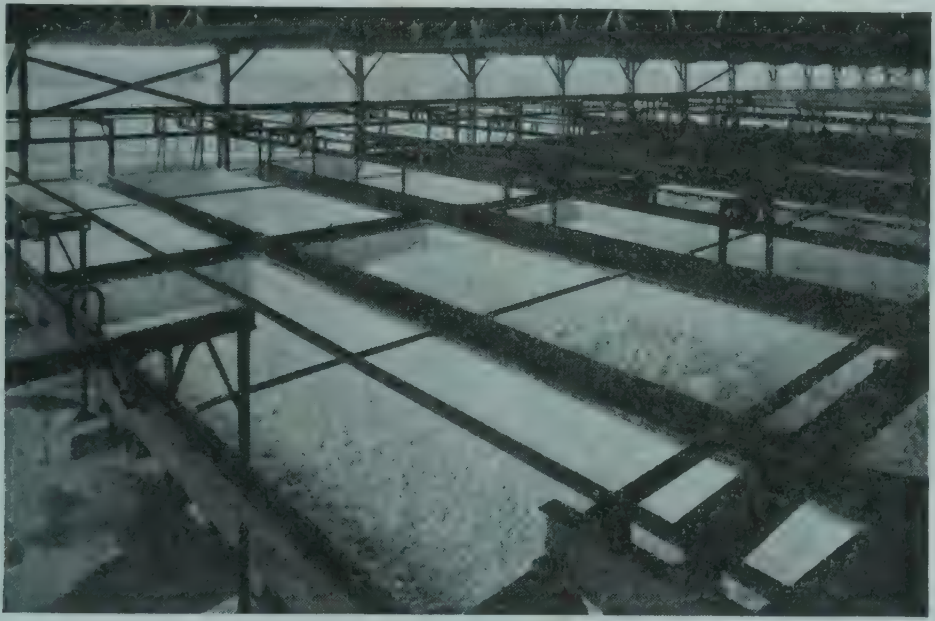

FIG. 16. Crystallization tanks in the works of a European potash mine. Hot, concentrated solutions of purified potash salts are run into these tanks. The pure potash salts crystallize out as the water evaporates and cools.

In the extraction of potassium chloride from the brines of Searles Lake, California, more complicated phase rule systems are involved. A remarkably effective research program in which the equilibria data were obtained for the various systems arising, established the chemistry of the "Trona Process" on a firm foundation. It represents a valuable con tribution by chemistry to the industrial and agricultural life of the country.[29, 58, 71, 74]

Flotation Methods. The application of physical ore-dressing methods to the refining of potash salts was an outstanding achievement, the first instance of such methods being employed in refining water-soluble materials. The basic research, reported in 1935, was conducted by the United States Bureau of Mines in cooperation with one of the potash companies in the New Mexico field.[14, 74] Most potash companies are now using such methods in at least a part of their refining operations. The technical and patent literature indicates that European operators also are using these methods at least to some extent.

FIG. 17. Evaporators at potash refinery, Trona, Calif.

Sylvinite when crushed breaks along the cleavage lines of its two component minerals, sylvite, and halite. While the two minerals differ slightly in specific gravity, the sylvite being the lighter of the two, little or no advantage may be taken of this. The crushed minerals are suspended in a solution saturated with respect to KCl and NaCl, and a small quantity of a reagent is added to film one of the minerals (see Figure 18). There are a number of reagents, among them the sulfated aliphatic alcohols and straight-chain alkyl amines, which will selectively coat one of the minerals. The particles that are coated attach themselves to air bubbles and are floated off either over vibrating tables or by frothing. The process is rapid and easily controlled, the small quantity of reagent required makes it economical, the precentage of recovery of the KCl is high, and the purity of the product is highly satisfactory, under proper controls running over 98 per cent pure KCl.

The Cross Method. A method of mining and recovering potassium chloride by dissolving the raw salt in the natural deposit and pumping it to the surface has been patented by Roy Cross.[19] The method is being tried by a company near Carlsbad, New Mexico, and some years ago was tried but later abandoned by one of the large producers in the same area. A well is dug to the potassium-bearing stratum; a large pipe is put down this well and a smaller pipe within the larger one. A heated solution saturated with respect to sodium chloride is passed down the outer pipe. When this comes in contact with the potash salt deposit the potassium chloride is dissolved. Forcing further quantities of mother liquor down the outside pipe forces the potassium chloride-saturated solution up the inside pipe. This is then cooled to remove the KCl in much the same manner as the crystallization methods described above.

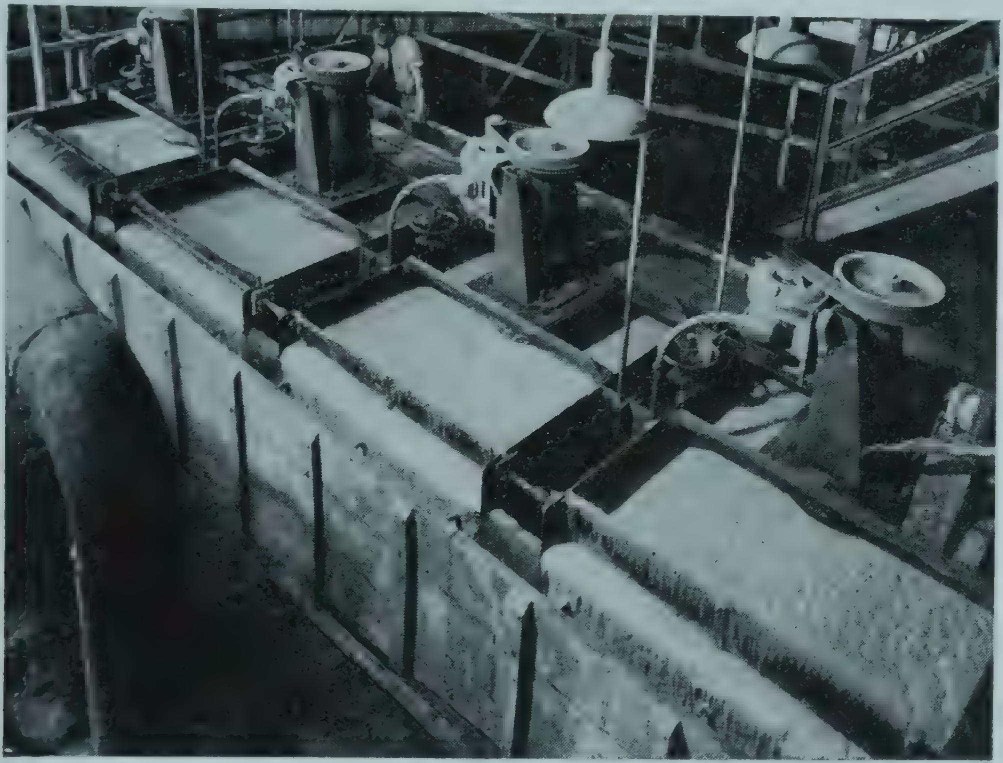

Fig. 18. Flotation cells for concentrating potassium chloride in sylvinite.

Such a method of extracting potash from subsurface deposits has the advantage of eliminating costly shaft construction, as well as mining operations. It is also supposed to permit the working of strata too narrow to be exploited by normal mining operations. At this time the method is still considered to be in the experimental stage.

Manure Salts. Manure salts may be the raw potash minerals as mined or mixtures of the raw minerals and muriate of potash. The potash content varies from 20 to 40 per cent K_2O, practically all in the chloride form. The impurities present will vary with the source, but NaCl will dominate, with varying quantities of $CaSO_4$, $MgCl_2$, $MgSO_4$, and clay.

The manure salts of American origin are for the most part raw sylvinite containing 22 to 26 per cent K_2O. The 30 per cent manure salts of European origin that were on the market before World War II were usually raw sylvinite, but sometimes Hartsalz or carnallite beneficiated with muriate of potash, to produce the desired K_2O content. The 20 per cent manure salts were much the same as the 30 per cent salts, except for the lower potash content. The term 20 per cent manure salts was dropped in 1930, substituting the term *High-Grade Kainite*. The 40 per cent manure salts are the raw minerals beneficiated with muriate of potash, or else a partially refined muriate of potash. This grade is popular in Europe but is seldom found on the American market.

Kainite. Kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) was among the first of the mineral potash fertilizers to be used. It usually contains NaCl as an impurity so that its theoretical K_2O content of 19 per cent is reduced to 12 to 16 per cent. The excellent results it gave as a fertilizer earned it great popularity both in Europe and North America.

Kainite is a secondary mineral formed by the action of water on carnallite and kieserite.[28, 34] It occurs in the mines of the Stassfurt area of Germany, but very little in the other known potash deposits in the world. Due to its mode of formation, it is in the upper zone of potash strata, and most subject to breaking in of surface water. Following several disasters of this nature, the mining of the mineral was greatly reduced and finally almost completely halted by 1920.

The great popularity of kainite as a potash fertilizer led to other potash salts of equal potassium content being sold under this name. At first it was guaranteed to contain a minimum of 12.4 per cent K_2O. Later a 14 per cent grade was introduced, the lower grade being dropped from American price lists in 1930. In 1928 the term High-Grade Kainite began to be applied to the 20 per cent manure salts, and in 1935, the importers dropped quotations on all grades lower than the 20 per cent high-grade kainite.

Sylvinite. The raw sylvinite ($KCl \cdot NaCl$) may be ground and sold under that name. It usually contains around 20 per cent K_2O. The term is used in France for the 20 per cent salts but has never been used much on the American fertilizer market, although a large part of the manure salts and high-grade kainite sold really is sylvinite.

Sulfate of Potash. Sulfate of potash is the principal nonchloride form of potash fertilizer. Its higher cost per pound of potash limits its use largely to those situations where, due to soil conditions or the requirements of the crop, a fertilizer low in chlorine is desired. Pure potassium sulfate contains 54 per cent K_2O, but the material on the fertilizer market usually contains 48 to 52 per cent K_2O, with the tendency in recent years for the content to approach the higher figure. By definition of the Association of American Fertilizer Control Officials, and most state fertilizer laws, no more than 2.5 per cent chlorine may be present if the material is to be sold as sulfate of potash.

Until the recent development of the langbeinite deposit in New Mexico, practically all the sulfate of potash was manufactured from KCl. In Germany the presence of kieserite in many of the potash deposits served as a source of the SO_4 The reaction takes place in two stages:

$$2KCl + 2MgSO_4 = K_2SO_4 \cdot MgSO_4 + MgCl_2$$
$$K_2SO_4 \cdot MgSO_4 + 2KCl = 2K_2SO_4 + MgCl_2$$

Sulfuric acid also can serve as a source of the SO_4, with the reaction as follows:

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl$$

This method of preparation is used in France and to some extent in the United States.

Sodium sulfate as a component of burkeite as well as potassium chloride can be recovered from the brine of Searles Lake in California. Sulfate of potash is being prepared by reacting these two products together under appropriate conditions according to the reaction:

$$2KCl + Na_2SO_4 = K_2SO_4 + 2NaCl$$

In one of the potash mines in New Mexico, the mineral langbeinite ($2MgSO_4 \cdot K_2SO_4$) is found in sufficient thickness and purity to permit its economical mining.[33] This thus represents a source of sulfate of potash in a natural form. By treating a solution of the mineral with KCl, the $MgSO_4$ is transformed into K_2SO_4, two steps being employed to permit higher recovery of K_2SO_4.

$$2(K_2SO_4 \cdot 2MgSO_4) + 2KCl + 18H_2O \rightarrow 3(K_2SO_4 \cdot MgSO_4 \cdot 6H_2O) + MgCl_2$$
$$3(K_2SO_4 \cdot MgSO_4 \cdot 6H_2O) + 6KCl \rightarrow 6K_2SO_4 + 3MgCl_2 + 18H_2O$$

During World War II, the $MgCl_2$ resulting from this reaction was utilized as a source of magnesium metal.

The extensive polyhalite deposits in Texas and New Mexico suggested that they might serve as a natural source of sulfate of potash.[82] This mineral has the composition $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$. Turrentine[74] points out that the high solubility of the potassium and magnesium sulfates, and the low solubility of calcium sulfate would appear to offer a simple means of separating these constituents. In practice, however, when the solution process begins, all three salts go into solution. The solubility product of the calcium sulfate or a complex containing it is soon reached, with consequent precipitation as a coating on the remaining material, thus preventing in a most effective manner the further dissolving of the magnesium and potassium.

The U. S. Bureau of Mines investigated three methods for the utilization of polyhalite.[17, 38] In all of these, the raw mineral is first washed to remove the sodium chloride. In calcination methods, the polyhalite is calcined at 500° C., thereby rendering the calcium sulfate insoluble. The potassium sulfate may then be removed by extraction with warm water. The second method of attack involves treatment to precipitate the calcium and magnesium, either with ammonia and carbon dioxide, or lime, leaving the K_2SO_4 in solution. The third process reduces the polyhalite to sulfides and oxides by treatment with carbon monoxide and/or hydrogen, separating the K_2S by solution and recovery by treatment with CO_2 to form K_2CO_3. At the present time, polyhalite is not being used, so it would appear that none of the methods will compete with other methods for obtaining potassium sulfate.

Potassium sulfate can be prepared also from the mineral alunite, which has the formula $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 3Al_2O_3 \cdot 6H_2O$. Rather extensive deposits in Utah, containing 8–10 per cent K_2O, have been exploited to some extent, but usually the main objective has been to produce aluminum, with sulfate of potash as a by-product.[36, 72] A number of processes have been reported utilizing this mineral.[6, 45] In most of these, the alunite is heated to 500–600° C., and dissolved in a solution of dilute H_2SO_4 and K_2SO_4 to produce a potassium alum. This is dried and heated breaking down according to the reaction:

$$K_2SO_4 \cdot Al_2(SO_4)_3 = K_2SO_4 + Al_2O_3 + 3SO_3$$

The K_2SO_4 is removed by leaching and the Al_2O_3 is used to produce metallic aluminum. Some commercial production, especially by the "Kalunite" process, has taken place, but for only short periods of time, indicating inability of the process to compete with other methods of producing sulfate of potash and aluminum.

Wyomingite. Large deposits of wyomingite in the state of Wyoming offer a potential source of potash fertilizers.[72] Leucite is the specific potassium-bearing mineral present. It has the formula $KAl(SiO_3)_2$ and the naturally-occurring material contains about 10 per cent K_2O. Various processes have been devised for the extraction of the potash based either on the use of sodium carbonate from wells near the wyomingite or treatment with acids. The end products will be KCl, KNO_3, KH_2PO_4, K_2CO_3, or K_2SO_4, depending on the process employed. It has been proposed to combine with this the production of phosphoric acid, permitting the preparation of potassium phosphate. Aluminum is produced along with the potash to help bear the cost of the production, but so far no process has been able to operate on a commercial basis under prevailing market conditions. The large leucite deposits of Italy have been used as a source of potash and aluminum, but apparently with only indifferent results, commercially.

Sulfate of Potash-Magnesia and Langbeinite. The German producers prepare a double sulfate of potash and magnesia by treatment of potassium chloride with kieserite. It really is the first step in the preparation of sulfate of potash by the kieserite method as explained above. As marketed it contains about 25 per cent K_2O and 9–12 per cent MgO. This material in years past was called double manure salts, and in Europe is called Patent Kali.

One of the mines near Carlsbad, New Mexico, is producing the mineral langbeinite ($K_2SO_4 \cdot 2MgSO_4$).[81, 33] Due to its slowness of solution, it is easy to wash out the NaCl impurity and market the material for direct use as a fertilizer. It contains about 22 per cent K_2O and 18 per cent MgO. Both of these potash fertilizers are particularly useful where potash in the sulfate form and soluble magnesium are desired.

Georgia Shale. The Georgia shales or Cartersville slates contain about 8 per cent potash in the form of a hydrous silicate of aluminum, iron, potassium, and other bases. Some work has been done on the extraction of potash from these soft shales, but costs of processes and utilization of by-products are stumbling blocks.[73]

Polyhalite. The polyhalite deposits in Texas have led to the suggestion that the mineral might be used directly as a fertilizer.[26] Their potash content is low, around 13–15 per cent K_2O, of which one-third to three-quarters is soluble in water as measured by ordinary analytical methods. The potash is in the sulfate form, and some magnesium also is present ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$). Fraps found this material compared favorably with sulfate and muriate of potash when used as a source of potash in growing corn in pots. Because of its low potash content, shipping costs would present a problem, unless used near the point of production.

Greensand. Extensive deposits of greensand occur in a belt from New Jersey south to North Carolina, and also in Texas. These are of marine origin and contain the mineral glauconite, a hydrous silicate of potassium and iron. The potash content is frequently 6 to 7 per cent, and sometimes up to 2 or 3 per cent or more P_2O_5 is present.[16, 27, 68] In New Jersey the material is at or near the surface, becoming deeper to the south. While the potash is not soluble in water, it slowly becomes available to plants. Large quantities have been used as fertilizer, especially during the middle and latter part of the last century. Numerous methods for the treatment of the greensand to extract and concentrate the potash have been tried on a small scale, but apparently are not commercially feasible under present conditions. In most cases by-products would result from the processes, frequently in such quantities as to present marketing problems. Greensand represents an extensive and possibly important potash reserve.

Wood Ashes. Wood ashes probably are the oldest form of potash fertilizer, having been used from time immemorial. The potash content varies from none to 25 per cent K_2O, depending on the source and the amount of leaching to which the ashes have been subjected. The potash is in the carbonate form. Calcium carbonate up to 30 per cent and some phosphoric acid also are present.

Tobacco Waste. The stems, ribs, and cuttings of tobacco that are waste products in tobacco manufacture are used as fertilizer, usually in mixed goods where they act as a conditioner as well as carrier of plant nutrients. They contain 4 to 10 per cent K_2O, largely as salts of organic acids.[16, 30, 73]

Wool Waste or Suint Potash. The dried sweat of sheep that accumulates on wool must be removed before spinning. This is called suint and contains 1 to 5 per cent potash, largely in the chloride form.[16]

Flue Dusts. The flue dusts from cement works contain about 10 per cent K_2O, largely in the sulfate form, with some carbonate.[73] Blast furnace dusts vary considerably in potash content, from none to 20 per cent K_2O, with most of them running less than 5 per cent. A small amount of potash is recovered each year from cement flue dust but little or none from blast furnace dusts.

Potash from Sugar and Alcohol Industries. Waste products from the production of alcohol from sugar cane molasses contain potash which can be recovered. The material is ashed, the resulting product containing about 33 per cent K_2O, largely in the sulfate form, but with some carbonate and chloride also present. It appeared on the Baltimore market for many years under the name of vegetable potash, but is no longer being produced.

Steffens waste from the sugar beet refineries can be evaporated to yield a material containing 10–12 per cent K_2O and about 5 per cent nitrogen. The potash is in the carbonate, sulfate, and chloride forms.[73] Little or no potash has been produced from this source in the United States since 1928.

Cotton Hull Ashes. Cotton hull ashes contain 20–35 per cent potash, if unleached. It is mostly in the carbonate form and these ashes are much sought after by tobacco growers, who usually are willing to pay a premium for them.

Seaweeds and Kelp. Seaweed and kelp contain 1 to 3 per cent potash on a wet basis and up to 30 per cent on a dry basis. They are used along seacoasts in many countries, and have served as a source material for the preparation of muriate of potash.[73, 77]

Potassium Metaphosphate. Potassium metaphosphate is a glassy-like material prepared by the reaction of potassium chloride and phosphoric acid in electric furnaces. It has the formula $K_4(PO_3)_4 \cdot H_2O$, is only slightly soluble in water, but both the potassium and phosphorus are available to plants. The experimental material that has been prepared contained about 40 per cent K_2O and 60 per cent P_2O_5.[16] It is not as yet in commercial production as a fertilizer.

Berliner has prepared an excellent and exhaustive bibliography on potash.[10] Details on the occurrence of deposits and production of potash fertilizers are well covered by Turrentine[73, 74] Krische[46] and Fulda.[28] Data on production and commerce in potash are given in the potash chapter in the Minerals Yearbook of the U. S. Bureau of Mines. Deliveries and importation of potash in North America and prices of potash and other fertilizers are published periodically by the American Potash Institute, Inc., Washington 6, D. C.

BIBLIOGRAPHY

1. Anonymous, "Les Mines de Potasse dans La Haute Alsace." Extrait du Bulletin de la Société Industrielle de Mulhouse (1912).
2. Anonymous, *Chem. Eng.* **55**: 216 (1948).
3. Anonymous, *Chem. Eng.* **57**: 205 (1950).
4. Ayres, A. S., *Hawaii Agr. Expt. Sta. Tech. Bull.* 9 (1949).
5. Backman, J., "The Economics of the Potash Industry." Washington, D. C., Amer. Potash Inst. (1946).
6. Baroch, C. T., Hackwood, A. W., and Knickerbocker, R. G., *U. S. Bur. Mines R. I.* 3845 (1946).
7. Baver, L. D., *Soil Sci.* **55**: 121 (1943).
8. Bear, F. E., "Soils and Fertilizers." 3rd ed. New York, John Wiley and Sons, Inc. (1942).
9. Bennett, H. H., "Soil Conservation." New York, McGraw-Hill Book Co., Inc. (1939).
10. Berliner, J. F. T., *U. S. Bur. Mines Bull.* 327 (1930).
11. Bray, R. H., *Soil Sci.* **58**: 305 (1944).
12. Brewer, A. K., *Ind. Eng. Chem.* **30**: 853 (1938).
13. Charrin, V., *Chimie et Ind.* **37**: 1225 (1937).
14. Coghill, W. H., De Vaney, F. D., Clemmer, J. B., and Cooke, S. R. B., *U. S. Bur. Mines R. I.* 3271 (1935).
15. Cole, L. H., *The Precambrian* **1** (June 1948).
16. Collings, G. H., "Commercial Fertilizers." Philadelphia, The Blakiston Co. (1947).
17. Conley, J. E., and Partridge, E. P., *U. S. Bur. Mines Bull.* 459 (1944).
18. Cramer, T. M., *Ind. Eng. Chem.* **30**: 865 (1938).
19. Cross, R., U. S. Pat. 2,331,890 (1943).

20. DeTurk, E. E., Wood, C. K., and Bray, R. H., *Soil Sci.* **55**: 1 (1943).
21. Direction Générale des Mines Dominiales de Potasse d'Alsace. "Rapport sur le Bassin de Potasse d'Alsace." Mulhouse, France (1947).
22. Dolbear, S. H., "Potash Reserves of the United States." Washington, D. C., Amer. Potash Inst. (1946).
23. Eckstein, O., *Trans. Third Int. Congress Soil Sci.* **1**: 186 (1935).
24. Eckstein, O., Bruno, A., and Turrentine, J. W., "Potash Deficiency Symptoms." Berlin, Verlagsgesellschaft für Ackerbau (1937).
25. Eckstein, O., Jacob, A., and Alten, A., "Arbeiten über Kalidüngung." Reihe 1 and 2. Berlin, Verlagsgesellschaft für Ackerbau (1931 and 1935).
26. Fraps, G. S., *Texas Agr. Expt. Sta. Bull.* **449** (1932).
27. Fraps, G. S., *Texas Agr. Expt. Sta. Bull.* **428** (1931).
28. Fulda, E., "Das Kali." II Teil. Stuttgart, Verlag von Ferdinand Enke (1928).
29. Gale, W. A., *Ind. Eng. Chem.* **30**: 867 (1938).
30. Garner, W. W., "The Production of Tobacco." Philadelphia, The Blakiston Co. (1946).
31. Greulach, V. A., *Texas Agr. Expt. Sta. Misc. Pub.* **13** (1946).
32. Hambidge, G. (Editor), "Hunger Signs in Crops." 2nd ed. Washington 5, D. C., Natl. Fertilizer Association (1949).
33. Harley, G. T., and Atwood, G. E., *Ind. Eng. Chem.* **39**: 43 (1947).
34. Harmer, P. M., and Benne, E. J., *Soil Sci.* **60**: 137 (1945).
35. Hermann, C., "Fortschritte in der Kali-Industrie." Dresden, Verlag von Theodor Steinkopff (1927).
36. Hild, J. H., *U. S. Bur. Mines R. I.* **3972** (1946).
37. Hilgard, E. W., "Soils." New York, The Macmillan Co. (1906).
38. Hill, J. R., and Adams, J. R., *Ind. Eng. Chem.* **23**: 658 (1931).
39. Hoar, H. M., *U. S. Dept. Commerce Trade Promotion Ser.* **33** (1926).
40. Hoffer, G. N., *Ind. Eng. Chem.* **30**: 885 (1938).
41. Hopkins, C. G., "Soils Fertility and Permanent Agriculture." Boston, Ginn and Co. (1910).
42. Jacob, A., "Die Gewinnung und Anwendung der Kalisalze." Newdamm, Verlag von J. Neumann (1939).
43. Kappan, H., "Die Bodenazidität." Berlin, Verlag von Julius Springer (1929).
44. Kitchen, H. E. (Editor), "Diagnostic Techniques for Soils and Crops." Washington, D. C., Amer. Potash Inst. (1948).
45. Knickerbocker, R. G., and Koster, J., *U. S. Bur. Mines R. I.* **3322** (1936).
46. Krische, P., "Das Kali." I Teil. Stuttgart, Verlag von Ferdinand Enke (1923).
47. Lipman, J. G., and Conybeare, A. B., *N. J. Agr. Expt. Sta. Bull.* **607** (1936).
48. Lyon, T. L., and Buckman, H. O., "The Nature and Properties of Soils." 4th ed. New York, The Macmillan Co. (1943).
49. Magraw, R. M., *Ind. Eng. Chem.* **30**: 861 (1938).
50. Mansfield, G. R., *U. S. Geol. Survey Bull.* **727** (1922).
51. Marbut, C. F., "Soils of the United States." *U. S. Dept. Agr. Advance Sheets* **8** (1935).
52. Matthews, E. D., *Ga. Agr. Expt. Sta. Circ.* **127** (1941).
53. Mehring, A. L., and Vincent, G. V., *U. S. Dept. Agr. Circ.* **689** (1943).
54. Michels, W., and Przibylla, C., "Die Kalirohsalze." Leipzig, Verlag von Otto Spamer (1916).
55. Millar, C. E., and Turk, L. M., "Fundamentals of Soil Science." New York, John Wiley and Sons, Inc. (1943).

56. Miller, E. C., "Plant Physiology." New York, McGraw-Hill Book Co., Inc. (1931).
57. Miller, M. F., and Krusekopf, H. H., *Mo. Agr. Expt. Sta. Res. Bull.* **177** (1932).
58. Mumford, R. W., *Ind. Eng. Chem.* **30**: 872 (1938).
59. Nightingale, G. T., *Soil Sci.* **55**: 73 (1943).
60. Peech, M., and Bradfield, R., *Soil Sci.* **55**: 37 (1943).
61. Rice, G. S., and Davis, J. A., *U. S. Bur. Mines Bull.* **274** (1927).
62. Rohde, G., *Z. Pflanzenkrankh. Pflanzenschutz* **45**: 499 (1935).
63. Romaine, J. D., *Better Crops with Plant Food* **24**: 6 (1940).
64. Ross, A. F., Chucka, J. A., and Hawkins, A., *Maine Agr. Expt. Sta. Bull.* **447** (1947).
65. Sauchelli, V., *Better Crops with Plant Food* **32**: 10 (1948).
66. Sayre, C. B., *N. Y. Agr. Expt. Sta. 66th Ann. Rept.* **1947**, 56 (1948).
67. Scholl, W., and Wallace, H. M., *Agr. Chemicals* **4**(6): 34 (1949).
68. Shreve, R. N., *U. S. Bur. Mines Bull.* **328** (1930).
69. Smith, H. I., *Ind. Eng. Chem.* **30**: 854 (1938).
70. Smyser, W. L., *U. S. Dept. Commerce Ind. Ref. Serv.* **3**: 1 (1945).
71. Teeple, J. E., "The Industrial Development of Searles Lake Brine." New York, Chemical Catalogue Co. (1929).
72. Thoenen, J. R., *U. S. Bur. Mines R. I.* **3190** (1932).
73. Turrentine, J. W., "Potash." New York, John Wiley and Sons, Inc. (1926).
74. Turrentine, J. W., "Potash in North America." New York, Reinhold Publishing Corp. (1943).
75. Turrentine, J. W., "Past Consumption and Future (1950) Requirements of Potash Salts in American Agriculture." Washington, D. C., Amer. Potash Inst. (1946).
76. Turrentine, J. W., *Better Crops with Plant Food* **32**: 24 (1948).
77. Turrentine, J. W., and Shoaff, P. S., *Ind. Eng. Chem.* **11**: 864 (1919).
78. Van Slyke, L. L., "Fertilizers and Crop Production." New York, Orange Judd Publishing Co. (1932).
79. Volk, G. M., and Bell, C. E., *Fla. Agr. Expt. Sta. Bull.* **416** (1945).
80. Williams, A. J., *Can. Chem. Proc. Ind.* **31**: 410 (1947).
81. Wrege, E. E., and Dancy, W. B., *Chem. Ind.* **65**: 46 (1949).
82. Wroth, J. S., *U. S. Bur. Mines Bull.* **316** (1930).

Chapter IX

PHOSPHATE FERTILIZERS

C. A. Black and W. H. Pierre

Iowa State College, Ames, Iowa

Ever since they were first manufactured about one hundred years ago, phosphate fertilizers have formed the backbone of the American fertilizer industry. Moreover, phosphate fertilizers have constituted the most important chemical product used on American farms. In 1947, according to Jacob,[62] the farmers of continental United States used in fertilizers approximately 1,725,000 tons of available P_2O_5. This amount represents nearly 9 million tons of phosphate fertilizer or approximately half the total fertilizer tonnage. It represents a cost to farmers of about 250 million dollars annually.

The continued use of large amounts of phosphate fertilizers is, of course, ample evidence of the need and importance of phosphate in profitable crop production. Although soils are relatively low in total phosphorus, of even greater importance is the fact that only a small portion of the soil phosphorus is readily available to plants. Phosphate fertilizers not only increase crop yields on many soils but also make possible a wider choice of crops and the production of crops of improved quality and greater total value. By making possible the better growth of legumes, phosphate fertilizers indirectly improve the nitrogen and organic matter status of the soil, which in turn results in an improvement of soil structure and a better control of soil erosion. It is for these and other reasons that phosphorus is sometimes referred to as the key to permanent agriculture.

EFFECT OF PHOSPHORUS ON PLANT GROWTH AND DEVELOPMENT

Phosphorus occurs in both inorganic and organic forms in plants, and is an essential constituent of all cells. Nucleic acid is apparently the dominant form of organic phosphorus present in active plant cells, being found in both the nucleus and the cytoplasm. Phosphorus is essential for certain reactions involved in respiration processes and perhaps also in photosynthesis.

The most outstanding symptom of extreme phosphorus deficiency is a purple coloration of the leaves caused by anthocyanin pigments that apparently are produced because of sugar accumulation in the stunted, phosphorus-starved plants.[35] With apple trees, tobacco, and tomatoes, phosphorus deficiency causes the leaf petioles to make an abnormally acute angle with the stalk, but in other plants, such as oats and the common legumes, there is no particularly distinctive outward symptom of phosphorus deficiency.[51]

It is frequently stated that phosphorus is particularly effective in stimulating root growth, and indeed it has been found that with root crops such as turnips and mangolds, where the major portion of the weight of the mature crop is in the roots, phosphorus increases the root growth more than the top growth.[71, 134] With many crops, however, phosphate applications have been found to increase the growth of the aerial portion of the plant as much as if not more than the growth of the root.[47, 84]

The application of phosphate fertilizers to soils deficient in phosphorus has frequently been found to produce earlier maturity of grain and other crops. This earlier maturity may be of special benefit in the northern states where immature corn is often damaged by autumn frosts. Brooks[18] found in an experiment in Massachusetts that at harvest 79 per cent of the corn had matured on the phosphate-treated plots compared with 58.5 per cent on untreated plots. Corresponding figures for an experiment in North Dakota[98] were 43.6 and 35.8 per cent. In experiments with oats, Brieba and Nelson[17] found that the effect of phosphate applications on maturity is most marked only when there is a considerable increase in yield. If the oats are not deficient in phosphorus, the maturity is little affected.

The application of phosphate fertilizers may also produce some change in the nature of the crop produced. The phosphorus content of vegetable, forage, and grain crops has been found to be increased by as much as 50 per cent or more as a result of phosphorus fertilization.[12] These increases in phosphorus content may result in improved feeding value.[120] But, as with the hastening of maturity, the increases in phosphorus content are greatest on soils very deficient in phosphorus.[21] There is also some evidence that phosphate fertilization may have an indirect effect on crop quality.[54] In part this might be brought about through the effect of phosphorus on maturity and through its effect in producing normal and vigorous crop growth. This is a problem, however, that needs further investigation.

SOIL PHOSPHORUS

The total amount of phosphorus in soils is rather low—about one-half the amount of nitrogen and one-twentieth the amount of potassium. Lipman and Conybeare[73] estimated that the crop land of the United States contains on the average about 1240 pounds of phosphorus per acre to the plow depth. In most soils this is found largely in the inorganic form, but in Prairie, Chernozem and other soils high in organic matter as much as one-half or more of the total phosphorus in the plow layer may be found in organic compounds as a part of the soil organic matter.[101] The amount present in organic compounds decreases rapidly with depth, however, as shown in Figure 19.

Soils differ also in the kind and proportion of different inorganic and organic phosphorus compounds present, and it is largely because of these differences that soils vary so much in their need for phosphate fertilizers. The total amount of phosphorus in soils is, therefore, not a good criterion of the need for phosphate fertilizers.

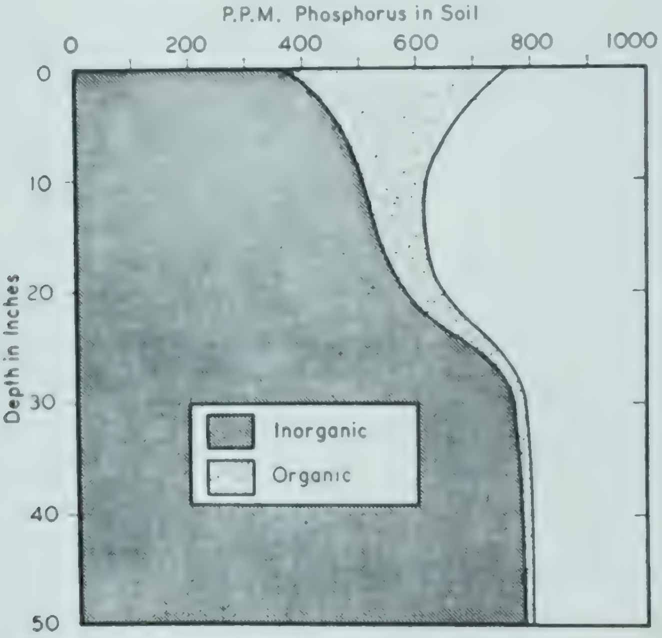

FIG. 19. Vertical distribution of inorganic and organic phosphorus in Marshall silt loam, a Prairie soil in western Iowa.[101, 102]

Losses from Soils. Losses of phosphorus from soils take place almost entirely through crop removal and through erosion. Unlike many other nutrient elements, phosphorus losses by leaching are negligible. This is explained by the low water-solubility of the soil phosphate compounds, the soil solution of most soils containing less than 0.1 p.p.m. of inorganic phosphorus.[105]

That considerable amounts of phosphorus are lost from the farm when crops are sold is indicated by the quantities of phosphorus present in various crops (Table 72). When crops are fed to animals, phosphorus is lost through the sale of the animals or animal products. Moreover, large losses of phosphorus also occur from manures under most farm conditions. The phosphorus removed by crops constitutes, of course, the most readily available phosphorus of the soil. It is not surprising, therefore, that even in soils of high inherent fertility phosphorus deficiencies have often become evident after less than fifty years of cropping.

On soils having rolling topography, the losses by erosion may be much greater than by crop removal.[86] The phosphorus removed by erosion includes much phosphorus that is present in relatively unavailable compounds. Both the percentage and the solubility of the phosphorus in eroded soil material are higher, however, than in the residual material.[108] This is because the fine soil particles, in which the phosphorus is concentrated, are more easily removed by wind and water than the coarser soil particles. Moreover, the availability to plants of phosphorus in the surface horizon of soils is ordinarily much greater than that in the lower horizons.[121] For these reasons it is not surprising that eroded soils are usually deficient in phosphorus and require greater amounts of phosphate fertilizers than do soils that have undergone little erosion.

TABLE 72. THE PHOSPHORUS CONTENT OF COMMON CROPS

Crop	Phosphorus Content[1] %	Average Acre Yield[2]	Phosphorus in Average Acre Yield lbs.
Corn: Grain	0.43	29.0 bu.	6.1
Stover	0.15	2700 lb.	3.6
			9.7 Total
Soybeans: Grain	0.78	18.6 bu.	7.9
Straw	0.16	2900 lb.	4.2
			12.1 Total
Wheat: Grain	0.40	14.6 bu.	3.1
Straw	0.08	1800 lb.	1.3
			4.4 Total
Oats: Grain	0.34	31.5 bu.	3.1
Straw	0.11	1200 lb.	1.2
			4.3 Total
Rice: Grain	0.36	48.8 bu.	6.9
Straw	0.13	2800 lb.	3.2
			10.1 Total
Cotton: Lint	0.054	245.6 lb.	0.1
Seeds	0.75	550 lb.	3.6
Stems, Leaves, Burs	0.14	1400 lb.	1.7
			5.4 Total
Sugar beets: Roots	0.11	12.6 tons	5.5
Leaves	0.22	2700 lb.	5.2
			10.7 Total
Potatoes: Tubers	0.25	126.2 bu.	4.0
Tobacco: Leaves	0.27	937.3 lb.	2.2
Alfalfa	0.27	1.97 tons	9.5
Red clover	0.22	1.13 tons	4.4

[1] Expressed on the dry weight basis and taken in the main from the average results given by Beeson.[12]

[2] Yields are U. S. averages for 1937–1941 except for alfalfa and red clover (mixed hay data) which are for 1930–1941.[11] The yields are given on the air-dry basis except for those of sugar-beet roots and potatoes which are on the fresh-weight basis. The yields of stover, straw, and seeds are estimates compiled from various sources.

Phosphorus Added in Fertilizers. Although the economical use of phosphate fertilizers cannot be determined on the basis of the amounts of phosphorus lost from the soil by cropping and erosion, it is of interest to compare the amounts of phosphorus added in fertilizers with the estimated amounts removed in crops and returned in manure. According to Cummings,[29] there were 742,000 tons of phosphorus in the harvested portion of the crops grown in the United States in 1943. In the same year, 550,000 tons of phosphorus were added in fertilizers. Thus, for the country as a whole, 74 per cent as much phosphorus was used in fertilizers as was removed in harvested crops. In addition to the phosphorus contained in commercial fertilizers there were about 200,000 tons of phosphorus in the manure applied on American farms in 1943.[29] Thus, the removal of phosphorus by cropping was essentially balanced by the additions of phosphorus to the soil.

The distribution of phosphorus removed in crops and the phosphorus applied in fertilizers is, of course, not uniform over the entire country. In 1943 the five Corn Belt states (Ohio, Indiana, Illinois, Iowa, and Missouri) removed in harvested crops over 30 per cent of the quantity of phosphorus removed by crops in the entire country and used only 14 per cent of the phosphate fertilizer. On the other hand, the seven southeastern states (Virginia to Mississippi, inclusive), which used over 40 per cent of all the phosphorus fertilizer applied, removed in harvested crops only about 8 per cent of the total phosphorus removed.

The large additions of phosphorus in fertilizers in some states as compared with the amounts removed in harvested crops is explained by the heavy rates of fertilization used on such crops as tobacco, citrus, potatoes, and truck crops. Since these crops occupy only very limited acreages, much of the crop acreage even in these states receives less phosphorus in fertilizers than is removed by crops. When erosion losses are considered the discrepancy becomes even greater.

KINDS OF PHOSPHATE FERTILIZERS AND THEIR PRODUCTION

Phosphate Rock. The source of practically all the phosphorus used in the fertilizer industry is phosphate rock or phosphorite, the principal phosphatic constituent of which is a mineral of the apatite group.[56] The P_2O_5 content of the higher-grade rocks generally used varies from about 25 to 35 per cent.

The most extensive deposits of phosphate rock are found in the United States and in the U.S.S.R., as indicated in Table 73. About half the known world reserves of phosphate rock are found in the United States. The State of Idaho contains the largest deposits with an estimated 6.4 billion tons, and Florida contains the second largest deposits with an estimated 5.7 billion tons.[78] Smaller deposits are found in Utah, Montana, Tennessee, Wyoming, Arkansas, South Carolina, and Kentucky, the quantity decreasing in the order named.

The heaviest user of phosphate rock in the prewar period was Europe. Virtually the entire quantity was imported from other countries since Europe is without large phosphate deposits. North America (mainly the United States) was the second heaviest user, and the U.S.S.R. was third. In the United States, most of the phosphate rock deposits now being commercially exploited lie in the southeastern states where the major portion of the phosphate is used. The western deposits are largely untouched.

TABLE 73. ESTIMATED WORLD RESERVES OF PHOSPHATE ROCK AND THEIR ANNUAL UTILIZATION

Area	Estimated Reserves of Phosphate Rock, tons [129][1]	Utilization of Phosphate Rock, 3-Year Prewar Average, tons[130]
North America	14,885,763,000	3,464,860
U.S.S.R.	8,342,291,000	1,308,761
Europe	-	6,014,479
Africa	3,876,277,000	249,120
Asia	-	1,106,268
Oceania	154,324,000	1,120,598
South America	-	4,850

[1] Unestimated deposits of phosphate rock occur in Brazil, Canada, China, Mexico, Palestine, and Poland.

The process of mining differs with the nature and location of the deposit. In most cases, however, the deposits being used lie near the surface of the land and are worked from the surface after removal of the overburden of soil materials. After the phosphate rock has been separated from most of the impurities, it is generally ground in preparation for marketing.

Phosphate rock itself that is ground finely enough for about 80 per cent to pass a 300-mesh screen finds some use as a fertilizer. The solubility of phosphorus in phosphate rock is quite low, which limits its availability to crops, but the cost of preparation is lower than is that of the other phosphate fertilizers, and ground phosphate rock can be sold at a lower price. According to Johnson and Tucker,[64] 411,543 tons were used for direct application to the soil in the United States in 1945. This quantity represents about 10 per cent of the quantity of phosphate rock used for the production of superphosphates.*

Superphosphate.† The addition of sulfuric acid to phosphate rock produces superphosphate (formerly known as acid phosphate), a product containing phosphate in a water-soluble form. The reaction between the phosphate rock and the acid may be illustrated as follows:

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* For world statistics on phosphates and superphosphates through 1942, see Gray,[48] and for U. S. statistics through 1929, see Jacob and Shelton.[63] Recent data may be found in the current Minerals Yearbook.

† See Parrish and Ogilvie[99] for a discussion of superphosphate production.

$$Ca_{10}F_2(PO_4)_6 + 6\ H_2SO_4 = 3\ Ca(H_2PO_4)_2 + 6\ CaSO_4 + CaF_2$$

In practice, the cheaper grades of sulfuric acid containing about 60 to 70 per cent acid are mixed with ground phosphate rock and the mixture is allowed to "cure" for some time. The heat produced from the reactions causes the volatilization of some water and fluorine compounds. The monocalcium phosphate and calcium sulfate produced in the reaction absorb water from the mixture, thus aiding the drying process. According to Hill and Hendricks[58] the anhydrous form of calcium sulfate is usually the main form present in ordinary commercial superphosphate, but the mono and dihydrate may occur also. Ordinarily superphosphate contains 16 to 22 per cent P_2O_5 and is about one-half calcium sulfate.

Ordinary superphosphate makes up the major proportion of chemically-processed phosphates because of the abundant supplies of low-cost sulfuric acid and the simplicity and cheapness of the manufacturing process. According to Jacob,[62], 9,140,000 tons of ordinary superphosphate (basis 18 per cent P_2O_5) were produced in the United States in 1947. This quantity of fertilizer represented 86.6 per cent of the total domestic production of available P_2O_5 in chemically processed fertilizers.

Concentrated Superphosphate.* A superphosphate containing approximately twice the P_2O_5 content of ordinary superphosphate is produced by adding phosphoric acid to phosphate rock. The reaction may be illustrated as follows:

$$Ca_{10}F_2(PO_4)_6 + 12\ H_3PO_4 = 9\ Ca(H_2PO_4)_2 + CaF_2$$

Two different methods are used for producing the phosphoric acid, namely, the wet process and the furnace process. In the wet process, phosphate rock is treated with an excess of sulfuric acid. Since sulfuric acid is a stronger acid than is phosphoric acid and since calcium sulfate is relatively insoluble, the phosphoric acid remains free and can be separated from the calcium sulfate by decantation and filtration.[27, 95] The furnace process involves the smelting of a mixture of phosphate rock, silica, and coke. The phosphate rock is decomposed and phosphorus is volatilized. The phosphorus is either converted directly into phosphoric acid or condensed and converted into acid in a subsequent operation.

Concentrated superphosphate usually contains 40 to 50 per cent available P_2O_5, 17 to 22 per cent CaO, and 2 to 6 per cent SO_3, whereas ordinary superphosphate contains 16 to 22 per cent available P_2O_5, 27 to 30 per cent CaO, and 29 to 31 per cent SO_3.

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* Concentrated superphosphate is variously known as double superphosphate, triple superphosphate and treble superphosphate. See Larison[70] for a general description of concentrated superphosphate production methods.

Concentrated superphosphate is second in importance among the chemically processed phosphate fertilizers. In 1947, 9.3 per cent of the total available P_2O_5 in such fertilizers was in the form of concentrated superphosphate, representing a quantity of 392,000 tons of material (basis 45 per cent available P_2O_5). The P_2O_5 content of ordinary and concentrated superphosphates made up 96.3 per cent of the total available P_2O_5 in chemically processed fertilizers in 1947.[62]

Basic Slag.* Basic slag is a by-product of the steel industry where lime added as a flux combines with phosphorus and other acid impurities. The more soluble phosphate compounds in basic slag are tricalcium phosphate, silicocarnotite ($5CaO \cdot P_2O_5 \cdot SiO_2$), and probably other silicate-phosphate materials of the nature of silicocarnotite but varying in the ratios of the constituents.[6, 16, 59] Most iron ores now being used in this country contain only a small amount of phosphorus as an impurity; hence, the basic slag produced has a low phosphorus content. An average analysis of this slag shows 8 to 10 per cent total P_2O_5 (as contrasted to 20 per cent P_2O_5 in high-grade European basic slag) and 50 to 60 per cent of calcium and magnesium oxides.

At present, less than 1 per cent of the world's production of basic slag comes from the United States. In 1938 the total U. S. production was 39.200 tons, all from the Birmingham, Alabama, iron district.[65] As the low-phosphorus iron ores currently used become depleted, the high-phosphorus ores, of which the United States has a considerable reserve, will come into general use. It is possible, therefore, that in the future basic slag will become a more important phosphate fertilizer in the United States.

Fused Tricalcium Phosphate. The process for producing fused tricalcium phosphate (formerly known as fused rock phosphate and now known to some extent as alpha tricalcium phosphate) consists of heating phosphate rock to 1500° to 1600° C. in the presence of water vapor.[30, 31] At these high temperatures (above the melting point of the rock), most of the fluoride is driven off. The presence of silica expedites the removal of the fluoride. A product called "calcined phosphate" has been prepared by defluorinating phosphate rock at about 1400° C., a temperature below the melting point of the furnace charge. The chemical nature of this material is similar to that of fused tricalcium phosphate.[59] Some phosphate rocks contain enough silica, but with others silica must be added. Silica helps also to prevent the reversion of phosphate to unavailable forms. When the fluoride has been removed from the rock, the phosphate cannot revert to the fluorapatite during cooling or subsequently. Nevertheless, rapid cooling of the product is necessary to leave the phosphate in the alpha tricalcium form and to prevent reversion to a less available form.[59, 79, *] Fused tricalcium phosphate contains about 30 per cent available P_2O_5. This fertilizer has been prepared on a small scale by the Tennessee Valley Authority, 24,000 tons being produced in the year ending June 30, 1947.[62]

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* For a more complete discussion, see Waggaman and Easterwood.[132]

Calcium Metaphosphate. In the process for producing calcium metaphosphate, the phosphorus-bearing gas obtained in the smelting of phosphate rock is burned to produce P_2O_5. This P_2O_5 is allowed to react with phosphate rock at an elevated temperature (about 1200° C.) to form the metaphosphate.[30] The reaction may be indicated as follows:

$$6\,P_2O_5 + Ca_{10}F_2(PO_4)_6 = 9\,Ca(PO_3)_2 + CaF_2$$

Some of the fluorine is volatilized during the treatment and some remains behind in the final product. Calcium metaphosphate is a concentrated phosphorus fertilizer. The average analysis of the metaphosphate made in 1941 showed a content of 60.6 per cent available P_2O_5.

Calcium metaphosphate has been produced on a limited scale by the Tennessee Valley Authority. For the year ending June 30, 1941, the amount of calcium metaphosphate produced was 11,447 tons.[30]

Potassium Metaphosphate. Potassium metaphosphate can be formed by the interaction of phosphoric acid and potassium chloride at high temperatures, by heating monopotassium phosphate and by smelting a mixture of coke, phosphate rock, and potassium silicate.[77, 112] The Tennessee Valley Authority has produced potassium metaphosphate on a small scale by burning phosphorus and allowing it to react at high temperatures with finely divided potassium chloride which is blown into the reaction chamber. Potassium metaphosphate is high in both phosphorus and potassium. When pure it contains 60.13 per cent P_2O_5 and 39.87 per cent K_2O. Potassium metaphosphate has been distributed by the Tennessee Valley Authority for testing in several states.

Other Phosphates. Several other kinds of phosphates are used for fertilizers, but at present only in small quantities. Liquid phosphoric acid is used in irrigation water in some of the western states, approximately 2000 tons of P_2O_5 being applied in this way in 1947.[62]

Ammonium phosphate is ordinarily prepared by mixing the desired proportions of ammonia and phosphoric acid or by treating phosphate rock with a mixture of sulfuric acid and ammonium sulfate. In 1944, 48,000 tons of ammonium phosphate were used in the United States.[81] This material may become of importance in the western states where the need is chiefly for a nitrogen-phosphorus mixture.

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[*] See the paper by Eisenberger et al.,[38] for a review of the chemistry of fused tricalcium phosphate production and numerous references to the literature.

Some ammonium phosphate is formed in the process of "ammoniation," by which is meant the addition of ammonia to superphosphate to form an "ammoniated superphosphate." (See Chapter VII.) While ammoniation is widely practiced and offers several advantages as a means of introducing nitrogen, there is a limit to the quantity of ammonia that can be used without decreasing the availability of the phosphate. As ammonia is added the monocalcium phosphate is converted first into dicalcium phosphate. As the quantity of ammonia is increased above about 2.5 per cent there is a rapid reversion to tricalcium phosphate.[68]

Phosphate rock-magnesium silicate glass is prepared by fusing phosphate rock with serpentine or olivine and quenching the melt with water. According to Jacob,[62] the first large-scale manufacture of this material in the United States was on the Pacific Coast in 1946. The results of tests with the fertilizer have not yet been published.

RESPONSE OF CROPS TO DIFFERENT PHOSPHATE FERTILIZERS

Much experimental work has been conducted to determine the relative increases in crop yields obtained with different phosphate fertilizers. Most of these comparisons have been between superphosphate and phosphate rock, although in recent years extensive studies have been carried on with the new phosphate fertilizers and phosphate compounds not yet in commercial production. In general, the more soluble the fertilizer the more available it is to crops. Thus, superphosphates and ammonium phosphate produce in general greater increases in crop yields per unit of phosphorus applied than do the less soluble phosphates—phosphate rock, basic slag, and tricalcium phosphates.

The results of many investigations show that the comparative value of different phosphate fertilizers depends also on (1) the nature of the soil, (2) the method of applying the fertilizer, and (3) the ability of the crop to utilize the phosphate applied. The type of soil to which the fertilizer is added may affect the relative value of various fertilizers in at least two ways. In the first place, the greater the acidity of the soil the more soluble and more available are the slightly soluble materials. Thus, the yield increases from applications of phosphate rock are generally greater on acid soils than on well-limed or alkaline soils. This is especially true when grass crops are grown. Secondly, when soluble phosphates are added to soils they react with the soil to form less soluble compounds. This reaction, known as "phosphorus fixation," varies with different soils. On soils having a high fixing power, the soluble phosphates are rapidly converted to less available forms. On acid soils high in fixing power the soluble phosphates have less relative advantage over the more insoluble forms of phosphate. If on such soils the phosphate is added in a slightly soluble form, the effect of fixation is relatively less important and the solubility of the fertilizer itself plays the dominant role in determining its availability. This is illustrated by the data in Table 74, which show the phosphate uptake by plants grown in quartz sand, Norfolk sandy loam, and Chester loam. The power of the substrates to fix added phosphate varied in the order named, quartz sand having the lowest fixing power and Chester loam the highest. The highest phosphate recovery from sand was obtained when the phosphate was added as the most soluble form, monocalcium phosphate. The highest recovery from Chester loam, on the other hand, was obtained from the least soluble form, tricalcium phosphate. Norfolk sandy loam was intermediate, giving the highest recovery from dicalcium phosphate. The relative availability of the different phosphates in each of the three cases was apparently determined by the balance between the solubility of the phosphate fertilizer and the fixation of the dissolved phosphate.

TABLE 74. PHOSPHORUS RECOVERED IN PLANTS FROM ADDITIONS OF DIFFERENT PHOSPHATES TO SAND AND SOILS [1]

	Recovery of Added Phosphorus by Rye Seedlings					
	Quartz Sand		Norfolk Sandy Loam		Chester Loam	
Source of phosphate [10 mg. P_2O_5 added per pot]	P_2O_5 mg.	Relative	P_2O_5 mg.	Relative	P_2O_5 mg.	Relative
Monocalcium phosphate	7.6	100	6.6	86	1.7	59
Dicalcium phosphate	4.7	62	7.7	100	1.9	65
Tricalcium phosphate	2.1	28	4.4	57	2.9	100

The method of applying the fertilizer is important because it affects both the fixation of soluble phosphates and the solubility of the less soluble phosphates. For this reason it has been found that, while the effectiveness of the former is favored by concentrating the fertilizer in bands, the effectiveness of the latter is favored by thorough mixing with the soil.

The nature of the crop grown also affects the value of the less soluble phosphate fertilizers such as ground phosphate rock. Bauer[9] and Bartholomew[7] found that sweet clover was able to utilize the phosphorus in phosphate rock to better advantage than were the other crops tested. Alfalfa, buckwheat, tobacco, turnips, and rutabagas have been shown to rate high also,[82, 128] whereas crops of the grass family (corn, wheat, rye, oats and barley, as examples) have been found in general to be poor feeders on phosphate rock.[9, 82, 128]

Superphosphate vs. Phosphate Rock Experiments. Field experiments in which superphosphate and phosphate rock have been compared on a phosphorus-equivalent basis generally show that superphosphate produces the larger yield increases. Many experiments have been made on the basis of an equal money value, with the phosphate rock supplying several times as much phosphorus as the superphosphate. Even here, the superphosphate is generally at an advantage on limed or on nearly neutral to alkaline soils. On the more acid soils, the phosphate rock is more soluble and is frequently equal to or superior to superphosphate.[10, 53, 92, 96, 107, 115, 137, 138, 139, 140]

Over long periods of time, the effectiveness of phosphate rock relative to that of superphosphate has been found in some cases to increase, as illustrated by certain experiments in Ohio,[115] Indiana,[138, 140] Kentucky,[106] Pennsylvania,[96] and Arkansas.[40] Such an increase might be expected on the basis of the greater amount of phosphorus generally added in the rock, if the phosphorus shows any noticeable availability a few years after it has been added. The larger the amount of phosphate added as phosphate rock, the greater should be the cumulative value with time, as suggested by the results of the Pennsylvania experiments in Table 75. The effectiveness of phosphate rock apparently has not increased with time in certain experiments in South Carolina.[20] It is important, therefore, in evaluating different phosphate fertilizers to take into account both the immediate and the residual effects. The more soluble phosphates, such as superphosphate, exert their maximum effect immediately, whereas the less soluble fertilizers, such as phosphate rock, may exert a more or less similar effect for several years or become slightly more available with time.[69, 106]

TABLE 75. RETURNS FROM SUPERPHOSPHATE AND PHOSPHATE ROCK APPLIED TO CROPS GROWN IN ROTATION[96]

Source of Phosphate	Pounds P_2O_5 Applied per Acre Each 4-Year Rotation	Relative Yield of Crops	
		1922-1929	1934-1941
Superphosphate	48	100	100
Phosphate rock	96	91	96
Phosphate rock	144	92	98
Phosphate rock	192	95	103

Experiments with New High-analysis Phosphates. The value of the newer types of phosphates has been studied in a rather extensive series of greenhouse and field tests carried out by the agricultural experiment stations in a number of states. The results of the greenhouse tests were summarized by Ross and Jacob,[110] who concluded that the availability of phosphorus in finely-ground calcined phosphate, calcium metaphosphate and fused tricalcium phosphate is about the same as that in monocalcium phosphate and superphosphate when the phosphates are used on neutral and acid soils. On an alkaline, calcareous soil from Arizona, monocalcium phosphate was most effective, superphosphate was second, and the other forms (calcined phosphate, fused tricalcium phosphate and calcium metaphosphate) were less effective. Since calcined phosphate and fused tricalcium phosphate are essentially tricalcium phosphate plus some apatite, these materials would be expected to be less effective on calcareous soils, particularly for grass crops.

The results of a large number of field tests comparing superphosphate, calcium metaphosphate, and fused tricalcium phosphate have been published under the auspices of the Coordinating Committee of the Valley States Land-Grant Colleges, the U. S. Department of Agriculture, and the Tennessee Valley Authority,[26] and the results of certain other tests have been summarized by Alway and Nesom.[3] A summary prepared by the Tennessee Valley Authority [124] of 758 experiments conducted in the seven Tennessee Valley States with cotton, corn, small grains, and hay shows that the yields with calcium metaphosphate averaged 99 per cent as high as with ordinary superphosphate. On calcareous soils and on certain acid soils where it is not well incorporated into the soil, calcium metaphosphate has been found to be inferior to superphosphate.[3, 49, 60, 97, 141] In 59 experiments with potassium metaphosphate summarized by the Tennessee Valley Authority,[124] the crop yields averaged 92.5 per cent as high as did the yields with superphosphate. A summary of the earlier experiment station work with fused tricalcium phosphate indicates that this fertilizer is somewhat less effective than superphosphate on acid soils. As a top dressing and on calcareous soils it has generally proved unsatisfactory.[3, 49, 127, 141] The more recent work indicates that on acid soils the material is of about the same value as superphosphate.[125] This difference is perhaps due to improved production methods used in more recent years. More attention has recently been given to the fluorine content and particle size of the product with efforts to determine the nature of material that will give the maximum benefit with the minimum of expenditure for fluorine removal and fine grinding.

While the more concentrated phosphorus fertilizers such as concentrated superphosphate, calcium metaphosphate, and fused tricalcium phosphate offer the advantage of lower transportation charges per unit of phosphorus, they have the possible disadvantage of containing no sulfur. Ordinary superphosphate contains a considerable quantity of calcium sulfate; hence, in fertilizers containing superphosphate, sulfur is applied automatically, serving to take care of possible deficiency of sulfur in the soil. A summary of 1060 experiments in the Tennessee Valley States [124] showed that the addition of sulfur with concentrated superphosphate produced a 5 per cent increase in the yield of cotton. On the other hand, 111 experiments with corn and 57 experiments with wheat showed no benefit from the additional sulfur. This again emphasizes the effect of differences in soils and in crops grown on the relative value of different phosphate fertilizers.

FIXATION OF PHOSPHATE FERTILIZERS

The fixation and availability of fertilizer phosphorus are controlled largely by the clay fraction of the soil. Ford[41] analyzed samples taken from an unfertilized plot and from a corresponding plot that had received a total of 140 pounds of phosphorus as superphosphate per acre over a number of years. He found that the phosphorus content of the sand fraction had not increased at all, that of the silt fraction had increased about 20 pounds per acre, and that of the clay fraction had increased about 100 pounds per acre. Most of the phosphorus fixed by the soil had therefore been retained by the clay fraction. Perkins, Wagoner and King[104] and others have likewise found that clay fixes more phosphate than do other separates in the soil. The fixation of phosphate by soils may be attributed mainly to reactions with four components, namely, the hydrous oxides of iron and aluminum, the clay minerals, calcium compounds, and the exchangeable cations, all of which are associated with the clay fraction.

As the acidity is increased through the range found in agricultural soils, the fixation of phosphate by hydrous oxides and by soils increases also.[37, 43] One explanation for this fact is the increased solubility and reactivity of aluminum and iron and the decreased solubility of the phosphates.[44, 66, 80] Stelly and Pierre[122] found that the naturally-occurring aluminum phosphates variscite and wavellite had a minimum solubility through the pH range of 5 to 6.5, and the naturally-occurring iron phosphate dufrenite had a minimum solubility through the pH range of 3.5 to 5.

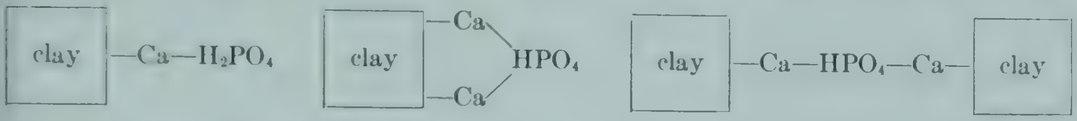
Phosphate fixation in acid soils cannot be attributed entirely to the hydrous oxides of iron and aluminum since there is evidence to indicate that certain of the minerals in the clay fraction of soils are capable of fixing phosphate. Murphy[88] found that kaolinite, a common soil clay mineral, is capable of fixing large quantities of phosphate, particularly after being finely ground in a ball mill. Stout[123] suggested that the phosphate replaces the hydroxyl ions on the exposed surfaces of the lattice sheets, yielding water and "kaolinite phosphate." Low and Black,[74] on the other hand, concluded that kaolinite reacts according to solubility-product principles, the product of the reaction being an aluminum phosphate.

Regardless of the mechanism of the reaction between kaolinite and phosphate, the reaction behaves like fixation by aluminum in that it is greatest under acid conditions. On the basis of the shape of pH-fixation curves, no distinction can be made between fixation by kaolinite and by hydrous aluminum oxides.[14, 37] Soil clays other than kaolinite have received insufficient study to clarify their behavior.

In soils that are alkaline, neutral or very slightly acid, phosphate is fixed largely by reaction with calcium. Phosphate that combines with calcium may be held in several different ways. Rapid fixation can take place to produce dicalcium and tricalcium phosphate. These compounds, however, are not stable under soil conditions and eventually must change to more basic forms. Bassett's [8] experiments indicated that the stable form of phosphate under conditions of slight acidity in soils might be hydroxyapatite. Further evidence to this effect was obtained by Schleede, Schmidt and Kindt [119] who found by X-ray photographs that a crystal structure characteristic of apatite was finally produced when various calcium phosphate compounds were given prolonged extraction with water.

The work of MacIntire and his associates indicates that the final stable form of phosphate fixed by soil calcium may be a secondary fluorapatite when a source of fluoride is present. According to MacIntire and Hatcher,[76] fluorapatite forms in mixtures of calcium fluoride and tricalcium phosphate, but not in mixtures of calcium fluoride and dicalcium phosphate. In agreement with these results, they found that calcium fluoride caused a decrease in the uptake of phosphate from soils by rye seedlings when the phosphate was supplied as tricalcium phosphate, but not when the phosphate was supplied as dicalcium phosphate. Fluoride-free superphosphate also was found to undergo reversion when mixed and aged with calcium silicate slag containing calcium fluoride. Since ordinary superphosphate contains the major portion of the fluoride that was present in the original phosphate rock, it already contains fluoride for reversion. Tricalcium phosphate is formed most rapidly under alkaline and slightly acid conditions; hence the reversion of superphosphate to fluorapatite is presumably most rapid in soils where these conditions obtain. In agreement with these considerations, pot experiments showed that the presence of calcium fluoride decreased the plant availability of fertilizer phosphorus to a greater extent on neutral soils than it did on acid soils. Evidence that fluorapatite forms in limed soils fertilized with superphosphate under field conditions was obtained by Nagelschmidt and Nixon.[89]

As a corollary to the formation of basic cation exchange salts shown by Bower and Truog,[15] it seems obvious that "cation exchange phosphates" should be formed upon the addition of soluble phosphate to soils. Allison [2] found that when hydrogen-saturated clays are titrated to a given pH value by the addition of calcium hydroxide and sodium hydroxide, the amount of phosphate retained by the calcium-hydrogen clay is greater than the amount retained by the sodium-hydrogen clay. Barbier, Chabannes and Miallet [5] obtained a similar contrast between calcium and potassium soils. This behavior is not entirely the result of calcium phosphate precipitation, because it takes place at pH values below those where calcium phosphate precipitates. Several different combinations may be visualized, as follows:



According to Barbier et al.,[5] the same type of compound forms with basic magnesium ions in the exchangeable form. It should form also with basic aluminum ions [100] and with basic iron ions.

FACTORS AFFECTING EFFICIENT USE OF PHOSPHATE FERTILIZERS

Of the various factors affecting the efficient use of phosphate fertilizers, those related to phosphorus fixation are often dominant. The soil reaction and the time of application, depth of application, and distribution of the phosphate through the soil are all factors that affect the fixation and availability of phosphate fertilizers, and all these factors are to some extent under the control of the farmer. The returns from phosphate fertilization are dependent also upon the favorableness of other soil and environmental factors for plant growth, and some of these likewise may be controlled by the farmer.

Soil Reaction. Strongly acid soils fix phosphate more strongly than do soils that are neutral or only slightly acid; hence, the availability of added soluble phosphate is lower in acid soils. On the other hand, as the pH of an acid soil is raised to near neutrality, the iron and aluminum phosphates hydrolyze to some extent and release phosphate. The reason for this behavior is the fact that at high pH values the hydrous oxides of iron and aluminum are less soluble than are the phosphates. Application of this principle has been made by Dean [33, 34] and Ghani and Islam,[46] who have found that phosphates fixed in acid soils are soluble in alkali extractants. When acid soils are limed, therefore, not only is the fixation of soluble phosphate diminished but also there may be some release of phosphate from originally insoluble forms.

In soils that are alkaline, neutral, or very slightly acid, phosphate is fixed largely by reaction with calcium, probably as hydroxyapatite and fluorapatite. Apatite is a rather stable mineral, as evidenced by the fact that it has been identified petrographically in the sand and silt fractions of a number of soils, some of which are strongly leached.[72, 75] Nevertheless, its solubility increases under acid conditions, as shown by Stelly and Pierre [122] and others. Phosphate availability has been increased by the addition of acids or acid-forming materials to soils that contain apatite phosphates,[23, 121] and doubtless the fixation of added phosphate would be decreased under these conditions. Strong acidification would, of course, bring into play the action of iron and aluminum. The most favorable soil reaction for maximum efficiency of added soluble phosphate fertilizers is in the range around neutrality.

Time of Application. Phosphate fixation in soils is not entirely an immediate reaction. The quantity of fertilizer phosphate in solution in the soil gradually decreases with length of time after application so that the availability becomes reduced. In Alabama, Searseth and Tidmore[118] found in a greenhouse experiment with a clay soil having high fixing power that superphosphate added 12 months before planting was only 5 per cent as effective in increasing the yield of plants as was the same amount added immediately before planting. Superphosphate added 30 days before planting was 80 per cent as effective as that added immediately before planting. Thorne[126] obtained similar but less striking results with Iowa soils having a lower fixing power. In general, therefore, soluble phosphate fertilizers are applied immediately before planting, because under these conditions the loss in availability from fixation is minimized.

Depth of Application. Since phosphate fertilizers do not move to any appreciable extent in the soil, it is important that the fertilizer be placed where it will be contacted by the roots of plants. Surface applications, or "top dressings," have been shown by many investigators to be less efficient than applications made at some depth in the soil.

Midgley[85] applied 20 per cent superphosphate at the rate of 500 pounds per acre to field plots, leaving some on the surface of the soil, mixing some with the surface 1½ inch, mixing some with the surface 3 inches and some with the surface 6 inches of soil. It will be noted from the results in Figure 20 that the corn and sudan grass, used as test crops, gave considerably greater increases in yield with the greater depths of incorporation. Moreover, sudan grass gave relatively more response at shallow depths of incorporation than did corn. Midgley noted that the roots of sudan grass were closer to the surface of the soil than were the roots of corn, apparently because the sudan grass was drilled (corn was planted in hills), thus shading the surface of the soil and keeping it more moist. Deep applications of phosphate, therefore, would appear to offer greater benefit in areas where the surface of the soil is dry during a considerable portion of the growing season. Striking benefits from deeper placement have been reported from Kansas[32, 83] under conditions of limited moisture.

Phosphate fertilization of permanent pastures and established stands of perennial legumes presents problems in application that have not yet been solved satisfactorily. In some cases the pastures are reseeded and limed at the same time the phosphate is applied. The phosphate and limestone are then usually drilled or disced into the soil. Where the land is too stony to be worked with tillage implements the phosphate must be applied broadcast as a top dressing. With top dressings, however, most of the phosphate is retained close to the surface of the soil, as indicated in Table 76. The degree of penetration depends not only on the fixing power of the soil but also on the soil moisture and rainfall conditions. If the phosphate comes in contact with moist surface soil or if the application is followed by a light rain that merely moistens the surface, the phosphate may be fixed almost entirely in the immediate surface of the soil. On the other hand, if the soil is dry and the application is followed by a good rain there may be substantial penetration into the soil,[57] before much fixation occurs. On sloping land, however, there may be marked loss of phosphate in the runoff.[109] If the fertilization program is repeated for a number of years there will, of course, be deeper penetration of the phosphate, as shown by the data of Bryan,[19] Chapman,[22] Hanley,[52] and others, but at best top dressing is a rather inefficient method of applying phosphate fertilizers.

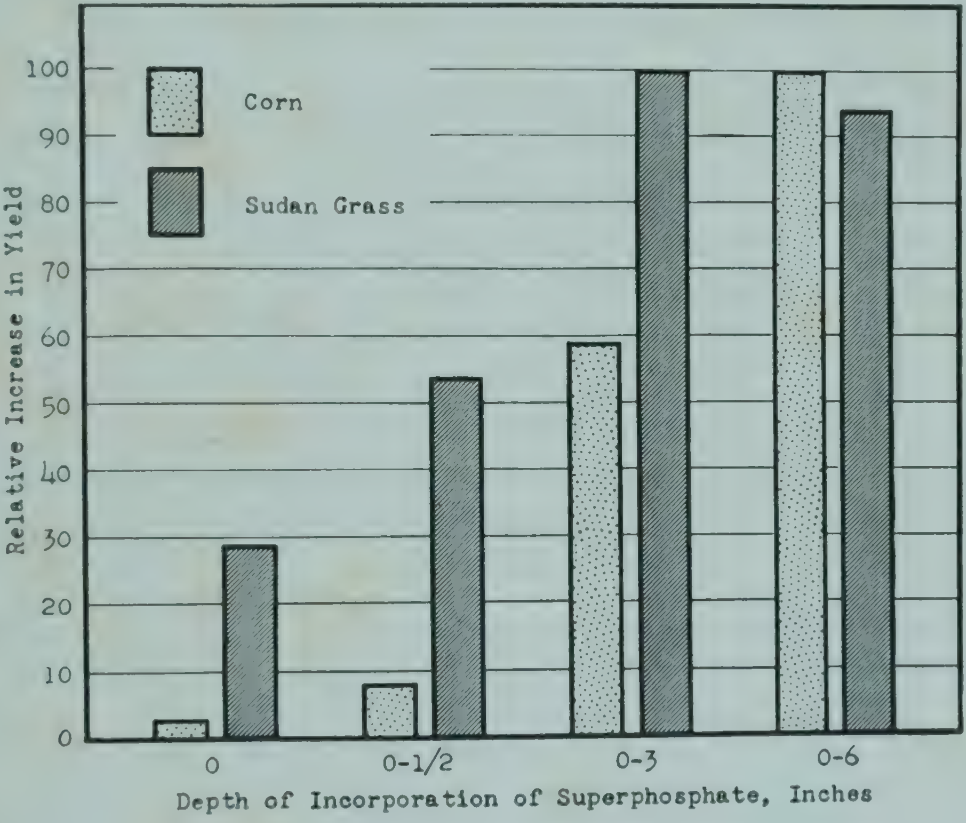


FIG. 20. Response of corn and Sudan grass to superphosphate incorporated to different depths in the soil.[85]

Distribution Through the Soil. The ideal situation for maximum yields would be to have an adequate supply of soluble phosphate distributed throughout the entire soil volume explored by plant roots. Few soils present this situation under natural conditions, and to produce it by application of phosphate fertilizer would require very large amounts of fertilizer on many soils because of loss by fixation. When a given amount of phosphate is mixed with the soil, the fixation that takes place is directly proportional to the quantity of soil used. Thus, if superphosphate is applied broadcast and is mixed well with the soil, the degree of fixation in unavailable forms will be greater than if the same amount of superphosphate is applied in a narrow band, in contact with only a portion of the entire soil. In the latter method of application the phosphate-fixing capacity of the soil around the band of fertilizer will be satisfied and a larger percentage of the added phosphate will remain in forms that can be utilized by crops.

Table 76. The Dilute-Acid-Soluble Phosphorus at Different Depths in Soil Under Permanent Pasture Receiving Top Dressing of Superphosphate[85]

Depth in Inches	Dilute-acid-soluble Phosphorus in Soil, P.P.M.[1] No Phosphate	300 Lb. Superphosphate	600 Lb. Superphosphate
0-0.5	10.0	54.0	100.0
0.5-1	4.0	14.0	38.0
1-2	3.6	5.0	8.0
2-3	4.0	4.0	3.6

[1] The superphosphate was applied on April 25 and the soil samples were taken on October 15.

Despite the fact that only a small portion of the crop roots contact the fertilizer, the placement of soluble phosphate in narrow bands or localized areas near the plant is generally the most effective way of applying soluble phosphate to crops. Figure 21 shows the results of an experiment with lettuce in Arizona[50] in which the effectiveness of band placement was compared with that of a broadcast application by varying the quantity of superphosphate applied in the band. In this experiment, 200 pounds of superphosphate applied in a band near the seed gave a slightly higher yield than did 400 pounds of superphosphate applied broadcast. With 400 pounds of superphosphate applied in a band the yield of lettuce was lower than it was with the 300-lb. application, perhaps owing to excessive salt concentration near the plants. Phosphates have less "salt effect" than do potassium and nitrogen fertilizers, but even with phosphates the placement of large quantities near to or in contact with the seed is likely to be injurious, particularly with sensitive crops such as peas and beans.[114]

Localized application is not of equal value with all types of phosphate fertilizers. With the less soluble fertilizers, fixation is not as great a problem as is solubility. It is obvious from solubility-product considerations that a larger quantity of phosphate will go into solution from a given quantity of slightly-soluble phosphate fertilizer if the fertilizer is distributed through a large volume of soil. This difference between fertilizers is well illustrated by Conner's [25] greenhouse experiments with three fertilizers on Crosby silt loam in which a comparison was made between mixing the fertilizers throughout the entire soil mass and placing the fertilizer in a concentrated layer. Layer placement was the better method with monocalcium phosphate, the most soluble of the fertilizers, but was much inferior with tricalcium phosphate, the least soluble of the fertilizers, as indicated in Table 77. The results with dicalcium phosphate, of intermediate solubility, showed a small decrease in effectiveness with the layer method of application. Whittaker et al.[136] have conducted similar greenhouse experiments, and White-Stevens [135] has reported the results of a field experiment with tomatoes in which it was found that band placement was superior to broadcasting with superphosphate, but broadcasting was superior to band placement with phosphate rock. Little attention has yet been given to field placement studies involving the newer phosphatic fertilizers such as calcium metaphosphate and fused tricalcium phosphate. As previously mentioned, however, these two materials have been found to be less effective than superphosphate when applied as a top dressing.

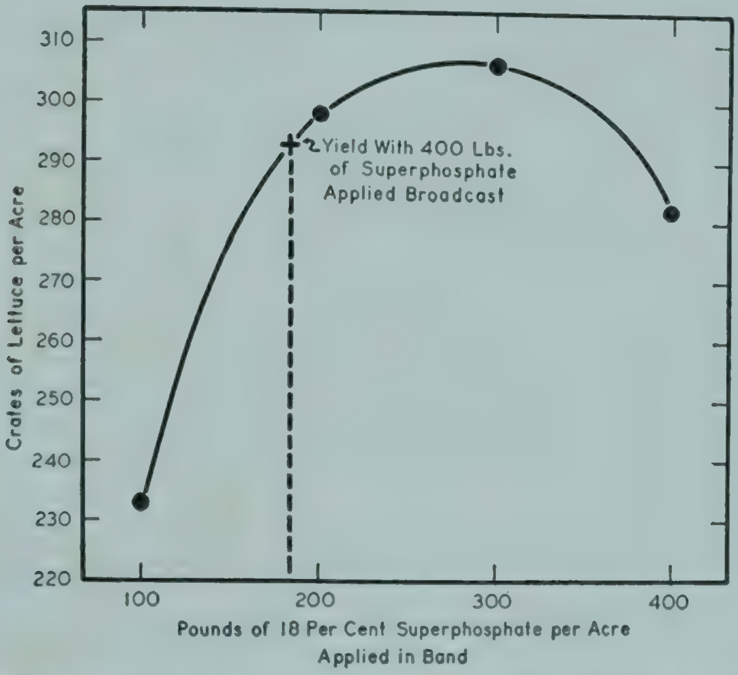


FIG. 21. Yield of lettuce with varying amounts of superphosphate applied in bands near the row in relation to the yield with 400 pounds of superphosphate per acre applied broadcast.[50]

Use of Granulated Phosphates. Granulated superphosphate offers some advantage over the usual material, which is a mixture of granules and powder, because to some degree the granulation insures localized placement and greater availability. Englehorn, Pearson and Stanford[39] found in greenhouse experiments that the efficiency of granulated superphosphates was equal to or greater than the efficiency of an equivalent quantity of powdered superphosphate. Fine granules had a greater immediate effect than did coarse granules, presumably because there were fewer coarse granules per unit volume of soil. The coarse granules, however, had a longer lasting effect, apparently because less of the phosphate was lost by fixation. Granulated superphosphates have been found to be superior to conventional superphosphates in several field experiments.[42, 116, 117] If this superiority is upheld by further experimentation, there will undoubtedly be a gradual change to the manufacture of granulated superphosphates. Another advantage of the granulated form is its free-flowing, dustless nature.

TABLE 77. THE INCREASE IN YIELD OF SUDAN GRASS ON CROSBY SILT LOAM WITH MONOCALCIUM, DICALCIUM AND TRICALCIUM PHOSPHATE APPLIED IN DIFFERENT WAYS[25]

Kind of Phosphate	Increase in Yield [Grams] with Indicated Method of Application	
	Layer	Mixed
Monocalcium phosphate	47	38
Dicalcium phosphate	31	35
Tricalcium phosphate	15	32

Level of Other Plant Growth Factors. In investigating the possible causes of the poor response of nonleguminous crops to phosphate on Mississippi soils known to be low in available phosphorus, Coleman[24] found that nitrogen deficiency was an important limiting factor. As shown in Table 78, the increase in yield from superphosphate application to oats and cotton was strongly dependent upon the quantity of nitrogen used in the fertilizer. With 48 pounds of nitrogen per acre the response to phosphate was about seven times as great as it was when only 16 pounds of nitrogen were applied. Similar results have been obtained in Iowa[91] and elsewhere.

TABLE 78. INCREASE IN YIELD OF OATS AND COTTON FROM SUPERPHOSPHATE AT TWO LEVELS OF NITROGEN IN FIELD EXPERIMENTS IN MISSISSIPPI[24]

Nitrogen Used in Fertilizer lb. per acre	Increase in Yield from 32 lb. P_2O_5 per Acre	
	Oats bu. per acre	Seed cotton lb. per acre
16	2.6	30
48	17.3	215

The response to added phosphate is, therefore, dependent not only upon the quantity of available phosphate already present in the soil but also upon the favorableness of other factors for plant growth. Thus, if soil moisture, potassium, nitrogen, or other nutrients are deficient, if soil aeration is poor, or if the weather conditions are unfavorable a relatively small response to phosphate will result.

Residual Effects of Phosphate Fertilizers

Largely because of phosphate fixation the recovery in crops of the phosphorus applied to soils in soluble fertilizers is relatively low. Ordinarily, not more than 25 per cent of the phosphorus added in soluble phosphate fertilizers is recovered by the crop during the first year. Most figures that have been reported run below 15 per cent.[28, 45, 67, 111]

Practically all the fertilizer phosphorus not recovered by the crop is fixed by the soil, very little being lost by leaching under usual conditions.[36, 87, 90] Some of this fixed phosphorus can be taken up by succeeding crops, but it is probably never completely removed from the soil.

The greatest effect of soluble phosphate fertilizers is ordinarily in the first year. In three experiments in England [113] in which superphosphate was applied to grass and hay, from 11 to 17 per cent of the 112 pounds of added P_2O_5 was recovered in the year of application with a gradual decline to a recovery of from 1 to 3 per cent in the fourth year. The total recovery of the added phosphate in the first four years ranged from 24 to 32 per cent.

Where heavy applications of phosphate are made over a period of years there is a considerable accumulation of total and available phosphorus in the soil. One of the first investigations on this subject was that of Anderson, Morgan and Nelson [4] in Connecticut, who found a marked rise in the phosphorus content of the soils of tobacco fields as the number of years the fields had been in tobacco increased. Similar results were obtained by Bryan [19] who analyzed the soils of citrus groves in Florida. These investigators believed that on such soils which had accumulated large amounts of phosphorus the quantity of phosphate used in the fertilizer might be reduced or perhaps even eliminated entirely for some time without any serious reduction in yield. Chapman [22] found that in California there had been considerable accumulation of phosphorus in the soil from heavy applications of phosphate to citrus groves. He concluded that the use of phosphate for citrus was unnecessary in that area because citrus trees were capable of making satisfactory growth on the native soil phosphate.

In Alabama, experiments with potatoes [133] and cotton [131] have shown that heavy applications of phosphate made over a period of several years have some cumulative effect on crop yields after the heavy applications are reduced or discontinued. In the experiment with cotton, superphosphate was applied annually for five years, after which the same rate of fertilization was continued on some plots, reduced on others and omitted entirely on still others. As shown in Figure 22 (constructed from the original data supplied by L. E. Ensminger), the plots that had received superphosphate at a rate equivalent to 60 pounds of P_2O_5 per acre annually during the preliminary five-year period suffered very little decline in yield during the ten-year residual period when the rate of application was reduced to 30 pounds of P_2O_5 per acre annually. There was a much greater decline in yields where the phosphate was omitted entirely, but these plots still produced considerably more cotton than did the check plots at the end of the ten-year residual period. The rapid decline in yields on the check plots that received no phosphate during the entire fifteen-year period is indicative of the residual effect of phosphate applied prior to the beginning of the experiments.

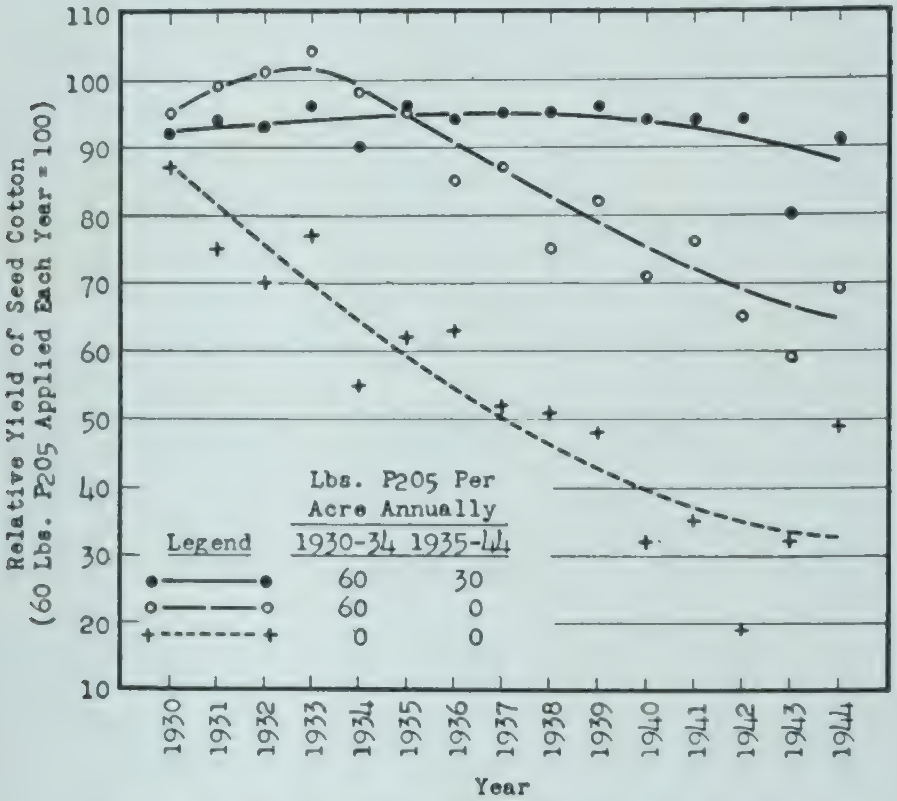


FIG. 22. Residual effect of superphosphate on yield of seed cotton.[131]

One additional point that might be noted in connection with the experiment on cotton is the fact that the efficiency of a given amount of fertilizer was greater when 30 pounds of P_2O_5 were applied annually for the ten-year period than it was when 60 pounds were applied annually during the first five years with none thereafter. Considering only the first ten years of the experiment, during which time 300 pounds of P_2O_5 had been applied, the total increase in acre yield of seed cotton was 4985 pounds where 30 pounds of P_2O_5 had been applied annually, and 4178 pounds where 60 pounds of P_2O_5 had been applied annually for each of the first five years.

More recently an extensive cooperative study of the phosphate status of soils of potato fields was made by several of the eastern State Agricultural Experiment Stations in cooperation with the U. S. Department of Agriculture.[29] The potato crop is a high-value crop that is usually heavily fertilized. Chemical analysis [103] showed that the surface soil of some of the fields had accumulated as much as a ton of P_2O_5 per acre, of which approximately 40 per cent was soluble in 0.002 *N* sulfuric acid (a reagent often used to estimate "available" phosphorus). Field experiments with potatoes in Maine and North Carolina [55, 93] on soils having varying levels of available phosphorus showed much lower response to phosphate on soils that had accumulated a large amount of phosphate. The average on the high-phosphate soils was about 10 to 15 pounds of potatoes per pound of P_2O_5 applied in the fertilizer compared with about 125 pounds of potatoes on the low-phosphate soils. The results of these experiments indicate that, even though long-continued fertilization has resulted in a large increase in phosphate in the soil, continued application of phosphate at a moderate rate may still produce small but profitable increases in yield of potatoes. Potatoes seem to be more dependent than are certain other crops, such as tobacco, cotton, and corn, upon the phosphate added in fertilizers, perhaps because of a less extensive root system.[94]

Under general farming conditions where much lower amounts of phosphate fertilizer are applied per acre, the amount of phosphorus that accumulates is much lower and the residual effect on the yields of succeeding crops is usually very small. Thus, in crop rotations where meadows are to be retained for several years, either relatively large amounts of phosphates must be applied at the time of seeding or smaller top-dressings of phosphate must be made every two to three years. The same is true of permanent pastures.

Needs and Potential Use

Although our farmers have used phosphate fertilizers for more than seventy-five years, the amounts now used are still inadequate from the standpoint of both efficient production and soil conservation. That conclusion was reached in 1944 by the State Production Adjustment Committees of the State agricultural experiment stations working in cooperation with the U. S. Department of Agriculture statisticians.[61] Their estimates of the amount of fertilizers that could be used profitably under generally prosperous economic conditions are that for the whole country nearly four times more phosphate fertilizer is needed than was used before the war (1935–1939) and more than twice as much as was used in 1944. The suggested increase over 1944 ranges from 25 per cent in the northeastern states to approximately 250 per cent in the Corn Belt and Lake States.

Although 8 Corn Belt and Lake States account for 47 per cent of the total suggested increase, compared to only 34 per cent for the 20 states of the Southeast, Appalachian, and Northeast regions, the increased needs in the latter states should not be minimized. Those states have large acreages of rolling and eroded soils that should be in permanent pasture or are now producing only scant and poor vegetation. Many field experiments have shown that phosphate and lime are the primary essentials in the establishment of a good vegetative cover of high quality legumes and grasses. According to Ibach,[61] less than 6 per cent of the permanent pasture in the humid region was fertilized in 1943.

The need for improving the phosphate status of many soils is also emphasized by the advances made in the development of better adapted and higher yielding crop varieties. It is evident that improved crop varieties make a greater demand on the soil for phosphorus and other elements than do lower yielding varieties, and that a higher phosphate level is necessary if full advantage is to be realized from crop improvement programs aimed at higher acre yields and greater efficiency in production.

Like other practices aimed at soil improvement and conservation and at greater efficiency in production, the practice of phosphate fertilization must be considered a part of a unified program of good soil management. Its place in this program varies with the soil, with the crop grown, and with the system of farming. It is a practice, therefore, that must be adapted to the individual farm.

BIBLIOGRAPHY

1. Allison, F. E., Pinck, L. A., and Sherman, M. S., *J. Am. Soc. Agron.* **33**: 918 (1941).
2. Allison, L. E., *Soil Sci.* **55**: 333 (1943).
3. Alway, F. J., and Nesom, G. H., *J. Am. Soc. Agron.* **36**: 73 (1944).
4. Anderson, P. J., Morgan, M. F., and Nelson, N. T., *Conn. Agr. Expt. Sta., Tobacco Sta. Bull.* **7** (1927).
5. Barbier, G., Chabannes, J., and Miallet, P., *Ann. Agron.* **16**: 7 (1946).
6. Barrett, R. L., and McCaughey, W. J., *Am. Mineral.* **27**: 680 (1942).
7. Bartholomew, R. P., *J. Am. Soc. Agron.* **20**: 913 (1928).
8. Bassett, H., Jr., *J. Chem. Soc.* **111**: 620 (1917).
9. Bauer, F. C., *Soil Sci.* **12**: 21 (1921).
10. Bauer, F. C., *Ill. Agr. Expt. Sta. Bull.* **405** (1934).

11. Becker, J. A., Froelich, P., Brandt, A. E., Larson, H. C., Mendum, S. W., Norman, T., Pollock, E. O., Rossiter, F. J., and Whalin, C. V., "Agricultural Statistics, 1942." Washington, D. C., U. S. Govt. Printing Office (1942).
12. Beeson, K. C., *U. S. Dept. Agr. Misc. Pub.* **369** (1941).
13. Beeson, K. C., *Bot. Rev.* **12**: 424 (1946).
14. Black, C. A., *Soil Sci. Soc. Am. Proc.* **7**: 123 (1942).
15. Bower, C. A., and Truog, E., *Soil Sci. Soc. Am. Proc.* **5**: 86 (1940).
16. Bredig, M. A., *Am. Mineral.* **28**: 594 (1943).
17. Brieba, R. S., and Nelson, L. B., Unpublished data. Iowa Agr. Expt. Sta. (1947).
18. Brooks, W. P., *Mass. Agr. Expt. Sta. Bull.* **162** (1915).
19. Bryan, O. C., *Soil Sci.* **36**: 245 (1933).
20. Buie, T. S., Currin, R. E., Kyzer, E. D., and Warner, J. D., *S. Carolina Agr. Expt. Sta. Bull.* **262** (1929).
21. Burke, E., Nygard, I. J., and Martin, W. M., *Montana Agr. Expt. Sta. Bull.* **280** (1933).
22. Chapman, H. D., *Calif. Agr. Expt. Sta. Bull.* **571** (1934).
23. Chapman, H. D., *J. Am. Soc. Agron.* **28**: 135 (1936).
24. Coleman, R., *J. Am. Soc. Agron.* **36**: 970 (1944).
25. Conner, S. D., *Am. Fertilizer* **81** (10): 9, 20, 22 (1934).
26. Coordinating Committee of the Valley-States Land-Grant Colleges, the United States Department of Agriculture, and the Tennessee Valley Authority. "Results of Cooperative Tests of Tennessee-Valley-Authority Plant-Food Materials by the Valley-States Land Grant Colleges. Part I. Agricultural Experiment Station Results." Mimeographed (1940).
27. Copson, R. L., Newton, R. H., and Lindsay, J. D., *Ind. Eng. Chem.* **28**: 923 (1936).
28. Crowther, E. M., *J. Roy. Agr. Soc. Engl.* **95**: 34 (1934).
29. Cummings, R. W., *Soil Sci. Soc. Am. Proc.* **10**: 240 (1946).
30. Curtis, H. A., *Tennessee Valley Authority Chem. Eng. Rept.* **1** (1942).
31. Curtis, H. A., Copson, R. L., Brown, E. H., and Pole, G. R., *Ind. Eng. Chem.* **29**: 766 (1937).
32. Davison, F., *Nat. Joint Comm. Fertilizer Appl. Proc.* **18**: 114 (1942).
33. Dean, L. A., *Soil Sci. Soc. Am. Proc.* **2**: 223 (1937).
34. Dean, L. A., *J. Agr. Sci.* **28**: 234 (1938).
35. DeTurk, E. E., *Ind. Eng. Chem.* **33**: 648 (1941).
36. Dyer, B., *U. S. Dept. Agr. Office Expt. Sta. Bull.* **106** (1902).
37. Eid, M. T., *M.S. Thesis, Ames, Iowa, Iowa State College Lib.* (1947).
38. Eisenberger, S., Lehrman, A., and Turner, W. D., *Chem. Revs.* **26**: 257 (1940).
39. Englehorn, A. J., Pearson, R. W., and Stanford, G., *Iowa Agr. Expt. Sta. Rept.* **1941**. Pt. I, 90–92.
40. Fine, L. O., and Bartholomew, R. P., *Soil Sci. Soc. Am. Proc.* **11**: 195 (1947).
41. Ford, M. C., *J. Am. Soc. Agron.* **24**: 395 (1932).
42. Franck, O., *Am. Fertilizer* **95** (1): 5, 22, 24; (2): 10, 24, 26 (1941).
43. Fudge, J. F., *J. Am. Soc. Agron.* **20**: 280 (1928).
44. Gaarder, T., *Vestlandets Forst. Forskssta. Medd.* **14** (1930).
45. Gericke, S., *Bodenkunde u. Pflanzenernähr.* **36**: 53 (1945).
46. Ghani, M. O., and Islam, M. A., *Soil Sci.* **62**: 293 (1946).
47. Goedewaagen, M. A. J., *Soil Sci.* **44**: 185 (1937).
48. Gray, A. N., "Phosphates and Superphosphates." London, E. T. Heron and Co., Ltd. (1944).

49. Green, J. R., *Montana Agr. Expt. Sta. Bull.* **356** (1938).
50. Griffiths, A. E., *Nat. Joint Comm. Fertilizer Appl. Proc.* **19**: 111 (1943).
51. Hambidge, G. (Editor), "Hunger Signs in Crops." Washington, D. C., American Society of Agronomy and National Fertilizer Association (1941).
52. Hanley, J. A., *Int. Grassland Congr. Rept.* **4**: 288 (1937).
53. Harper, H. J., *Oklahoma Agr. Expt. Sta. Bull.* **B–248** (1941).
54. Hartwell, B. L., *Nat. Fertilizer Assoc. Proc. Ann. Convention* **8**, Sec. 2 (1932).
55. Hawkins, A., *Soil Sci. Soc. Am. Proc.* **10**: 252 (1946).
56. Hendricks, S. B., Hill, W. L., Jacob, K. D., and Jefferson, M. E., *Ind. Eng. Chem.* **23**: 1413 (1931).
57. Hetterschij, C. W. G., *Phosphorsäure* **5**: 215 (1935).
58. Hill, W. L., and Hendricks, S. B., *Ind. Eng. Chem.* **28**: 440 (1936).
59. Hill, W. L., Hendricks, S. B., Jefferson, M. E., and Reynolds, D. S., *Ind. Eng. Chem.* **29**: 1299 (1937).
60. Hinkle, D. A., *J. Am. Soc. Agron.* **34**: 913 (1942).
61. Ibach, D. B., *U. S. Dept. Agr., Bur. Agr. Econ. F. M.* **52** (1946).
62. Jacob, K. D., *Fertilizer Rev.* **23** (1): 3, 19 (1948).
63. Jacob, K. D., and Shelton, W. A., *Nat. Fertilizer Assoc. Proc. Ann. Convention* **6**: 139 (1930).
64. Johnson, B. L., and Tucker, E. M., in "Minerals Yearbook, 1945." pp. 1391–1409. Washington, D. C., U. S. Govt. Printing Office (1947).
65. Johnson, B. L., and Warner, K. G., in "Minerals Yearbook, 1940." pp. 1301–1320. Washington, D. C., U. S. Govt. Printing Office (1940).
66. Karlsson, N., and Mattson, S., *Kgl. Lantbruks-Högskol. Ann.* **8**: 405 (1940).
67. Karraker, P. E., Miller, H. F., Bortner, C. E., and Todd, J. R., *Kentucky Agr. Expt. Sta. Bull.* **413** (1941).
68. Keenen, F. G., *Ind. Eng. Chem.* **22**: 1378 (1930).
69. *Kentucky Agr. Expt. Sta. Ann. Rept.* **59**: 24 (1946).
70. Larison, E. L., *Ind. Eng. Chem.* **21**: 1172 (1929).
71. Lawes, J. B., *J. Roy. Agr. Soc. Engl.* **8**: 494 (1847).
72. Leahey, A., *Scientific Agr.* **15**: 704 (1935).
73. Lipman, J. G., and Conybeare, A. B., *N. J. Agr. Expt. Sta. Bull.* **607** (1936).
74. Low, P. F., and Black, C. A., *Soil Sci. Soc. Amer. Proc.* **12**: 180 (1948).
75. McCaughey, W. J., and Fry, W. H., *U. S. Dept. Agr. Bur. Soils Bull.* **91** (1913).
76. MacIntire, W. H., and Hatcher, B. W., *Soil Sci.* **53**: 43 (1942).
77. Madorsky, S. L., and Clark, K. G., *Ind. Eng. Chem.* **32**: 244 (1940).
78. Mansfield, G. R., *Econ. Geol.* **35**: 405 (1940).
79. Marshall, H. L., Reynolds, D. S., Jacob, K. D., and Tremearne, T. H., *Ind. Eng. Chem.* **29**: 1294 (1937).
80. Mattson, S., and Karlsson, N., *Kgl. Lantbruks-Högskol. Ann.* **6**: 109 (1938).
81. Mehring, A. L., Wallace, H. M., and Drain, M., *U. S. Dept. Agr. Circ.* **756** (1946).
82. Merrill, L. H., *Maine Agr. Expt. Sta. Ann. Rept.* (1895). II. Rept. of Director, pp. 10–14 (1896).
83. Metzger, W. H., *Nat. Joint Comm. Fertilizer Appl. Proc.* **16**: 105 (1940).
84. Meyer, R., and Storck, A., *Z. Pflanzenernähr. Düng. Bodenk.* **10A**: 329 (1927).
85. Midgley, A. R., *J. Am. Soc. Agron.* **23**: 788 (1931).
86. Miller, M. F., and Krusekopf, H. H., *Missouri Agr. Expt. Sta. Res. Bull.* **177** (1932).
87. Morgan, M. F., and Jacobson, H. G. M., *Conn. Agr. Expt. Sta. Bull.* **458** (1942).

88. Murphy, H. F., *Hilgardia* **12**: 341 (1939).
89. Nagelschmidt, G., and Nixon, H. L., *Nature* **154**: 428 (1944).
90. Neller, J. R., *Soil Sci. Soc. Am. Proc.* **11**: 227 (1947).
91. Nelson, L. B., Lawton, K., and Black, C. A., *Soil Sci. Soc. Am. Proc.* **10**: 235 (1946).
92. Nelson, M., *Arkansas Agr. Expt. Sta. Bull.* **290** (1933).
93. Nelson, W. L., and Hawkins, A., *J. Am. Soc. Agron.* **39**: 1053 (1947).
94. Nelson, W. L., Krantz, B. A., Colwell, W. E., Woltz, W. G., Hawkins, A., Dean, L. A., MacKenzie, A. J., and Rubins, E. J., *Soil Sci. Soc. Am. Proc.* **12**: 113 (1948).
95. Newton, R. H., and Copson, R. L., *Ind. Eng. Chem.* **28**: 1182 (1936).
96. Noll, C. F., and Irvin, C. J., *Penna. Agr. Expt. Sta. Bull.* **423** (1942).
97. O'Brien, R. E., *Va. Agr. Expt. Sta. Bull.* **364** (1944).
98. Olson, P. J., and Walster, H. L., *J. Am. Soc. Agron.* **26**: 205 (1934).
99. Parrish, P., and Ogilvie, A., "Calcium Superphosphate and Compound Fertilizers." London, Hutchinson's Scientific and Technical Publications (1946).
100. Paver, H., and Marshall, C. E., *J. Soc. Chem. Ind.* (London) **53**: 750 (1934).
101. Pearson, R. W., and Simonson, R. W., *Soil Sci. Soc. Am. Proc.* **4**: 162 (1939).
102. Pearson, R. W., Spry, R., and Pierre, W. H., *J. Am. Soc. Agron.* **32**: 683 (1940).
103. Peech, M., *Soil Sci. Soc. Am. Proc.* **10**: 245 (1946).
104. Perkins, A. T., Wagoner, C. E., and King, H. H., *Soil Sci.* **53**: 37 (1942).
105. Pierre, W. H., and Parker, F. W., *Soil Sci.* **24**: 119 (1927).
106. Roberts, G., Freeman, J. F., and Kinney, E. J., *Kentucky Agr. Expt. Sta. Bull.* **397** (1939).
107. Roberts, G., Freeman, J. F., and Miller, H., *Kentucky Agr. Expt. Sta. Bull.* **420** (1942).
108. Rogers, H. T., *Soil Sci. Soc. Am. Proc.* **6**: 263 (1941).
109. Rogers, H. T., *Soil Sci. Soc. Am. Proc.* **7**: 69 (1943).
110. Ross, W. H., and Jacob, K. D., *J. Assoc. Off. Agr. Chemists* **20**: 231 (1937).
111. *Rothamsted Expt. Sta. Rept. 1930,* **43**.
112. Royster, P. H., Clark, K. G., Hignett, T. P., Bowe, L. E., Lansdon, H. I., Southard, J. C., and Turrentine, J. W., *U. S. Dept. Agr. Tech. Bull.* **543** (1937).
113. Russell, E. J., *Min. Agr. Fisheries (Engl.) Bull.* **28**, 3rd ed. (1939).
114. Salter, R. M., in "U. S. Dept. Agr. Yearbook," p. 546 (1938).
115. Salter, R. M., and Barnes, E. E., *Ohio Agr. Expt. Sta. Bull.* **553** (1935).
116. Sayre, C. B., *Nat. Joint Comm. Fertilizer Appl. Proc.* **12**: 39 (1936).
117. Sayre, C. B., *Nat. Joint Comm. Fertilizer Appl. Proc.* **12**: 117 (1936).
118. Scarseth, G. D., and Tidmore, J. W., *J. Am. Soc. Agron.* **26**: 152 (1934).
119. Schleede, A., Schmidt, W., and Kindt, H., *Z. Elektrochem.* **38**: 633 (1932).
120. Smith, G. E., and Albrecht, W. A., *Soil Sci. Soc. Am. Proc.* **7**: 322 (1943).
121. Stelly, M., Unpublished Ph.D. Thesis. Ames, Iowa, Iowa State College Lib. (1942).
122. Stelly, M., and Pierre, W. H., *Soil Sci. Soc. Am. Proc.* **7**: 139 (1943).
123. Stout, P. R., *Soil Sci. Soc. Am. Proc.* **4**: 177 (1939).
124. Tennessee Valley Authority. "Efficiency of TVA Phosphates." Unpublished manuscript (1945).
125. Tennessee Valley Authority. "Fused Tricalcium Phosphate (fused phosphate)." Rept. No. 3. Knoxville, Tenn., Tenn. Valley Authority (Mimeographed) (1945).

126. Thorne, M. D., Unpublished M.S. Thesis. Ames, Iowa, Iowa State College Lib. (1941).
127. Toevs, J. L., and Baker, O. G., *Idaho Agr. Expt. Sta. Bull.* **230** (1939).
128. Truog, E., *Wisc. Agr. Expt. Sta. Res. Bull.* **41** (1916).
129. *U. S. Dept. Agr. Misc. Pub.* **586** (1946).
130. United Nations Food and Agriculture Organization. "Report on World Food Situation. Tech. Supplement 7. Fertilizers." Washington, D. C., Food and Agr. Organization of the United Nations. Mimeographed (1946).
131. Volk, G. W., *J. Am. Soc. Agron.* **37**: 330 (1945).
132. Waggaman, W. H., and Easterwood, H. W., "Phosphoric Acid, Phosphates, and Phosphatic Fertilizers." New York, Chemical Catalog Co. (1927).
133. Ware, L. M., Brown, O., and Yates, H., *Proc. Am. Soc. Hort. Sci.* **41**: 265 (1942).
134. Watson, D. J., and Russell, E. J., *Empire J. Expt. Agr.* **11**: 65 (1943).
135. White-Stevens, R. H., *Nat. Joint Comm. Fertilizer Appl. Proc.* **20**: 88 (1944).
136. Whittaker, C. W., Coe, D. G., Bartholomew, R. P., Volk, G. W., and Rader, L. F., Jr., *J. Am. Soc. Agron.* **39**: 859 (1947).
137. Wiancko, A. T., Walker, G. P., and Ervin, S. E., *Purdue Univ. Agr. Sta. Circ.* **246** (1939).
138. Wiancko, A. T., Walker, G. P., and Hall, H. G., *Purdue Univ. Agr. Sta. Circ.* **243** (1939).
139. Wiancko, A. T., Walker, G. P., Miles, S. R., Bannwart, W., and Brunner, H., *Purdue Univ. Agr. Expt. Sta. Circ.* **248** (1939).
140. Wiancko, A. T., Walker, G. P., and Robbins, C., *Purdue Univ. Agr. Expt. Sta. Circ.* **244** (rev.) (1941).
141. Willis, W. P., Jr., and Harrington, F. M., *Montana Agr. Expt. Sta. Bull.* **369** (1939).

Chapter X

MIXED FERTILIZERS

S. F. Thornton

F. S. Royster Guano Co., Norfolk, Va.

Mixed fertilizers are manufactured products made by putting together two or more fertilizer materials. They are designed as carriers of readily available plant nutrients and are used to supplement soil supplies in filling the needs of growing crops.

General discussions of the production, properties, and use of mixed fertilizers are to be found in the writings of Andrews,[1] Bear,[2] Blair,[7] Collings,[8] Jacob and Mehring,[12] Lang,[15] Ross and Mehring,[36] Sauchelli,[37] and others. Such discussions necesarily are closely linked with discussions of fertilizer materials and of crop responses.

Mixtures versus Straight Materials

Both fertilizer materials and mixed fertilizers are used for direct application to the soil. In Europe the common practice is to apply separately the fertilizer materials required to supply the needed nutrients. In the United States, on the other hand, it is customary to depend largely on mixed fertilizers.

Varied explanations for the greater popularity of mixed fertilizers in the United States have been given. Andrews,[1] for example, suggests that it may be due to the fact that bird guano, the first fertilizer extensively used, contained all three principal plant nutrients—12 per cent nitrogen 10 per cent phosphoric acid, and 3 per cent potash. Guano proved to be an excellent fertilizer, and it is natural that attempts should have been made to simulate it in the form of artificial mixtures.

Actually, the origin of the custom of using mixed fertilizers appears rather obscure. It is well known, however, that it has continued and expanded until today approximately 70 per cent of all nitrogen, phosphoric acid, and potash used in the United States as fertilizer is applied to the soil in the form of mixtures and only 30 per cent, as straight materials. Convenience and efficiency appear to have been the chief factors responsible for the development of this practice.

In contrast to mixed fertilizers, most fertilizer materials contain only one of the principal plant nutrient elements. Even when a material does contain two or more of these elements, the proportion in which they are present usually is not the one best suited to the requirements of most crops and soils. Such needs, as a rule, are most effectively and most economically filled through the use of a mixture of two or more materials put together in accordance with a formula designed to provide the needed quantities of nitrogen, phosphoric acid, potash, and other plant nutrients.

Straight materials find their chief uses under soil and crop conditions where the supply of only one of the principal plant food elements needs to be increased and as supplements to mixed fertilizer to take care of unusual demands for one or more of these nutrients. Examples of such uses are the application of superphosphate to pastures, the side-dressing of corn with nitrate of soda and other nitrogenous fertilizer materials, and the broadcast application of muriate of potash on mucks and other soils having an abnormally high potash requirement.

The principal advantages that have caused the American farmer to continue to look with favor upon mixed fertilizers are as follows:

1. Better balance between nitrogen, phosphoric acid, and potash.
2. More adequate provision for secondary and minor plant nutrients.
3. Closer control of residual acidity and alkalinity.
4. Wider choice of analysis.
5. Convenience in handling.
8. Economy of application.
9. Improved drilling qualities.
10. Increased reliability.

THE MANUFACTURING PROCESS

The manufacture of mixed fertilizer had its beginning in a small plant in Baltimore, Maryland, in 1849. In the beginning it was a scavenger industry, concerned largely with collecting and processing waste materials.

In those early days the producers of mixed fertilizers took whatever materials they found readily at hand and attempted to compound them into mixtures suitable for use on the farm. The fertilizers produced were low in plant nutrient content, bulky, smelly, dark in color, and made up largely of plant and animal by-products and waste materials. Little was known of plant nutrient values and little attention was given to plant nutrient content.

In the one hundred years that have passed since the first ton of mixed fertilizer was produced, the industry has changed from a scavenger industry to one of the largest units of the heavy chemical industry. Total fertilizer consumption in 1947 exceeded 17,000,000 tons, and of this total approximately 12,000,000 tons was used in the form of mixed fertilizers.

At the present time in the neighborhood of 1000 factories are engaged in the production of mixed fertilizers. These factories vary in size from small mixing plants that purchase all of their raw materials from other producers and mix and ship only a few hundred tons each year, to huge factories that produce their own sulfuric acid and superphosphate and may ship in excess of 100,000 tons of mixed fertilizer in a single season.

The equipment used in factories producing mixed fertilizers varies over a very wide range. In the smaller plants it may be simple implements and machines—wheelbarrows, carts, portable screens and small mixing machines—designed primarily for use with hand labor. In the large and more modern factories there is likely to be found complicated arrangements for storing materials and for storing and curing mixtures, along with electrically operated machinery of all kinds for excavating, moving, crushing, grinding, and mixing materials and for transporting, screening, weighing, bagging, and loading the finished mixtures.

Into these factories, large and small, raw materials are gathered and stored against the time of need. As many as 10 to 12 of these different raw materials may go into the formulation of a single grade of mixed fertilizer.

In some factories it is common practice to make all mixtures up to the exact analysis desired in advance of shipping time and to store these mixtures in bins for curing and conditioning. When this practice is followed it is necessary when shipping time arrives only to crush, screen, and bag the prepared mixtures.

Other factories follow the practice of making "base goods" that consist of mixtures of two or more materials, such as sulfate of ammonia and superphosphate or muriate of potash and superphosphate. The bases so prepared are cured in piles and at shipping time blended with one another and with other nitrogenous, phosphatic and potassic materials in such a way as to produce the desired analysis. After mixing and screening, the mixtures go directly into bags for shipment.

Ammoniation is the most important accomplishment in mixed fertilizer technology of the past quarter century. Other significant accomplishments of this period are the production of double-strength fertilizers and of nonacid forming mixtures; granulation; recognition of the importance of secondary and minor elements; reduction in the number of grades sold; and a substantial increase in the average nitrogen, phosphoric acid, and potash content of all mixed fertilizers.

CHEMICAL CONTROL

Mixed fertilizer production has taken on the nature of a chemical process. Raw materials are largely chemicals, reactions are complex, and results difficult to predict in many cases. Strict chemical control is a necessary part of the manufacturing process all of the way from the selection of the raw materials to the shipping out of the finished goods.

Provisions for chemical control work vary widely with the different members of the fertilizer industry. Some have large central laboratories to which all samples are sent, others have a number of small laboratories located at strategic points to serve one or more factories, and still others depend on the service provided by commercial laboratories. Most of the large producers have their own laboratories, but many of the smaller ones do not.

In the factory, chemical control is concerned primarily with efficiency of production and control of quality. It supplies the analysis of the raw materials and provides a check on each step in the manufacturing process.

Effective production and quality control means getting good samples from the factory and returning the results of the investigation to the factory with the least possible delay. This is the end toward which all efforts are directed because each day, and often each hour, that the results are delayed decreases their value.

This requirement for speed is a dominant consideration in all plans for the chemical control laboratory—its location, its equipment, its staff, and its plan of operation. To a large extent each day's operation must be complete in itself.

Sampling is the most troublesome problem with which the control chemist has to deal. Other problems worthy of specific mention are the determination of secondary and minor plant nutrients, the investigation of new materials, the study of reactions in the fertilizer mixture, the analysis of concentrated mixtures, segregation, and reversion.

MATERIALS USED

Many different materials go into the production of mixed fertilizers. For convenience of discussion these varied materials may be divided, in accordance with their principal function in the mixture, into four groups as follows:

1. Suppliers of plant nutrients
2. Conditioners.
3. Neutralizers of residual acidity.
4. Fillers.

Suppliers of Plant Nutrients. Fertilizer materials are valuable in the mixture primarily because they supply plant nutrient elements—secondary and minor elements as well as nitrogen, phosphoric acid, and potash. Other functions are definitely secondary in importance to this primary role.

Nitrogen is supplied by an especially wide variety of materials, the most important of which are ammonia, ammonia solutions, sulfate of ammonia, ammonium nitrate, cyanamid, urea, process tankage, seed meals, and sewage sludge. Phosphoric acid comes largely from superphosphate and potash, from soluble potassium salts, principally chlorides and sulfates.

Calcium is obtained chiefly from superphosphate, gypsum, and limestone. Magnesium is supplied as a component part of dolomitic limestone, as magnesium oxide, as sulfate of potash-magnesia and as magnesium sulfate. Sulfur is provided as elemental sulfur; as gypsum; and as an essential constituent of other fertilizer materials, such as standard superphosphate, sulfate of potash and sulfate of ammonia.

The minor elements occur in small amounts as impurities in other fertilizer materials and, when required in larger quantities, are added as special materials. Boron is supplied largely as borax; copper, as copper sulfate; manganese, as manganese sulfate; and zinc, as zinc sulfate.

Conditioners. In the beginning mixed fertilizers were made up largely of low-grade organics and other relatively inert materials. Such mixtures gave little or no trouble from caking and remained in good drilling condition over long periods of time.

Fertilizer materials now in use are, to a large extent, concentrated and highly purified chemicals that readily react with one another. Conditioners are necessary to keep such mixtures in condition to drill nicely.

Conditioners in common use in mixed fertilizers are chiefly low-grade organic materials, such as peat, tobacco stems, peanut hulls, and rice hulls. Such materials usually are added at a rate of around 100 pounds per ton.

TABLE 79. QUANTITIES OF VARIOUS MATERIALS USED IN MIXED FERTILIZERS IN THE UNITED STATES IN 1945

Materials	Tons
Superphosphate	4,519,016
Muriate of potash	950,577
Sulfate of ammonia	779,488
Inert filler	597,213
Natural organics	527,597
Dolomite	475,000
Other potassic materials	270,314
Ammonia and ammonia solutions	219,899
Other chemical nitrogen	194,084
Other phosphates	142,356
Secondary and minor elements	125,000
Organic conditioners	70,000
Total	8,870,544

Neutralizers of Residual Acidity. Mixed fertilizers compounded with the nitrogenous materials currently in most common use tend to have a high residual acidity. Such acidity is objectionable for many crops and soils and makes necessary the addition of counteracting basic materials.[38, 39, 41]

Dolomitic limestone is the dominant basic material so used in fertilizer mixtures. Other basic materials of lesser importance are cyanamid, magnesium oxide, hydrated lime, high calcium limestone, and cocoa tankage.

Filler. There are many different materials from which a fertilizer of a given analysis may be made. After the materials required to furnish the desired quantities of plant nutrients are assembled and placed in the mixture, it often is necessary to add filler to complete the ton.

FIG. 23. A pile of superphosphate, cured and ready for use in compounding mixed fertilizers.

For most grades of mixed fertilizer now in common use the amount of "make-weight" material needed to bring the weight of the mixture up to an even ton will be less than 100 pounds. It is a necessary part of mixed fertilizer production because guarantees of plant nutrients in terms of fractions of a per cent are not permitted in most states.

Filler becomes objectionable in fertilizer mixtures only when used in excessive quantities, as in the compounding of low-grade mixtures, such as 2-12-6 and 3-8-5. Fortunately few such mixtures remain on approved grade lists, and these few give promise of disappearing in the very near future.

The common filler material used in fertilizer is sand. Also occasionally used are soil, ground coal ashes, and various other waste products.

In summary it seems desirable to list the principal materials used in mixed fertilizer as given by Mehring[22] for 1945. These data are given in Table 79. They clearly demonstrate the dominance of superphosphate as a fertilizer material and emphasize the importance of muriate of potash as a source of potash and of sulfate of ammonia and ammonia and ammonia solutions as carriers of nitrogen.

TABLE 80. APPARENT COMPOSITION OF THE AVERAGE MIXED FERTILIZER SOLD IN 1935

Substance	Per Cent
Calcium sulfate	18.62
Calcium phosphates	16.83
Organic matter	9.52
Ammonium sulfate	7.14
Sodium chloride	5.06
Potassium chloride	4.75
Potassium sulfate	4.34
Ammonium phosphates	3.15
Sodium nitrate	2.55
Aluminum sulfate	1.94
Iron sulfate	1.90
Calcium fluoride	1.44
Sodium sulfate	1.06
Magnesium chloride	0.72
Calcium cyanamide	0.70
Urea	0.07
Zinc sulfate	0.06
Manganese sulfate	0.05
Borax	0.03
Copper sulfate	0.02
Moisture	4.90
Dolomite	2.20
Acid insoluble	12.95
Total	100.00

This same general picture is presented by suggestions made by Mehring[22] as a result of his study of data showing the average composition of mixed fertilizers in 1935 as reported by Lundstrom and Mehring[16] in 1939. These suggestions, given in Table 80, show a large number of substances present in the average fertilizer mixture, with two components of standard superphosphate—calcium sulfate and calcium phosphates—occupying dominant positions. (See Figure 23.)

PHYSICAL AND CHEMICAL PROPERTIES

Aside from the content of plant nutrient elements, the principal characteristics of mixed fertilizers that influence efficiency are:

1. The uniformity with which they can be distributed in the field.
2. Their physical and chemical effects on the soil.
3. Their physiological effect on the crop.

Many properties play a part in determining these characteristics. Several of the more important ones are discussed briefly below.

Drillability. The uniformity with which a fertilizer can be distributed in the field is an important factor in determining efficiency. If the distribution is irregular some plants will get an over-supply while others suffer from a shortage. In addition to this the distribution of a fertilizer having a poor physical condition requires extra time and labor and may result in broken machinery.

The chief causes of poor drillability are caking and stickiness. To drill easily a fertilizer should be dry, free-flowing, and of medium particle size.

Caking usually finds expression in the formation of lumps or of a crust around the mass of fertilizer. In extreme cases the entire mass of material may be knit together in one solid lump. The causes of caking are many and by no means fully understood. Temperature changes, changes in moisture content, and chemical reactions between the component materials in the mixture appear to be the principal causes. Curing (Figure 24) improves drillability.

Stickiness appears to be definitely connected with high moisture content. Fertilizers made with high moisture contents and mixtures containing large quantities of hygroscopic materials that tend to take up large amounts of moisture from the air at ordinary humidities are likely to give trouble from stickiness.

Uniformity. Many materials having different physical properties go into the production of mixed fertilizers. Putting such materials together and keeping the mixtures uniform is a difficult job.

The attainment of complete uniformity in mixtures would be a costly process and usually is undesirable from an economic standpoint. The mixing machinery in a modern fertilizer factory, however, does a good job and when properly used gives mixtures of a satisfactory degree of uniformity.

Another problem in uniformity is segregation within the mixture after it has been prepared. Materials having different specific gravities and different particle sizes and shapes tend to change their original positions in the mixture when the loose mass is poured from one container to another or jarred or shaken during the operations necessary for packaging, transportation, and use.

With most mixed fertilizers segregation has not proved to be a serious problem. Experience has shown, however, that some mixtures do segregate to an important extent. Most troublesome in this respect are mixtures of nitrogen and potassium salts in which no superphosphate is used.

Residual Acidity and Alkalinity. Many nitrogenous materials are strongly acid-forming and, unless counteracted by other materials, their use results in the production of strongly acid-forming mixed fertilizers. Acid-forming fertilizers when applied in relatively large amounts and used year after year usually bring a sharp increase in soil acidity and often result in serious reductions in crop yields. Such acidity increases are especially pronounced on the lighter, more sandy soils.

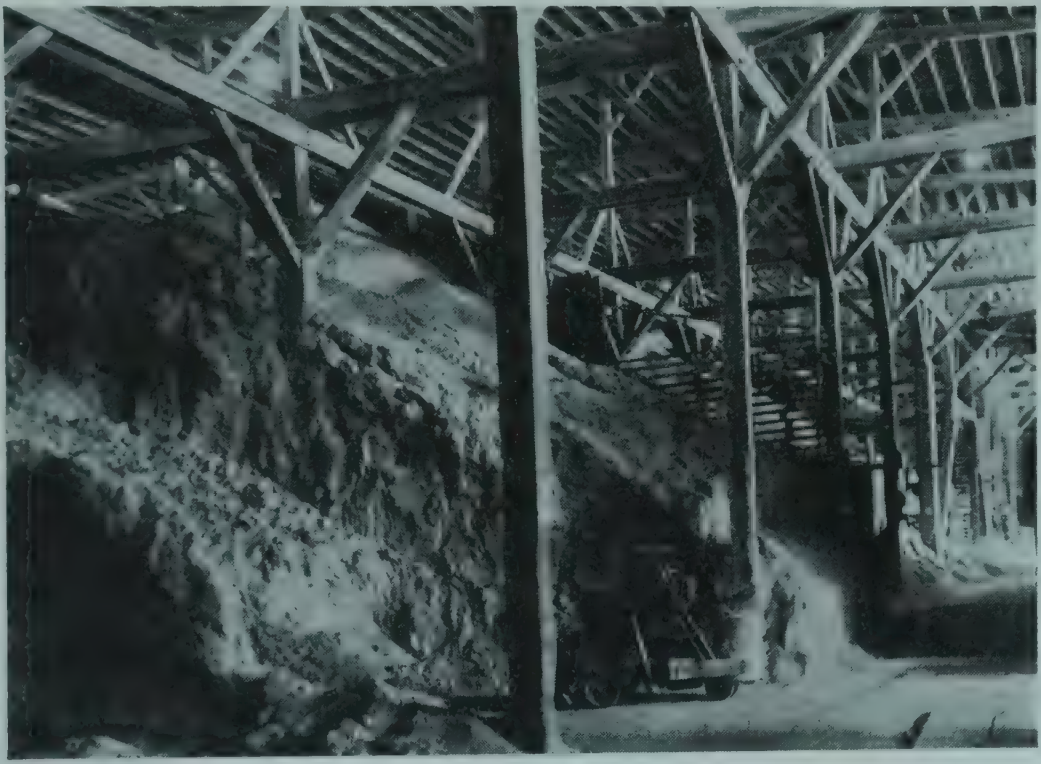


FIG. 24. Mixed fertilizer made to grade and cured and conditioned in the factory to give improved drilling condition on the farm.

On the other hand, an increase in soil acidity may improve the productiveness of an alkaline soil or may make any soil more suited to the needs of some particular crop. Under such conditions the use of acid-forming fertilizers may become a desirable practice.

In the early days of mixed fertilizer production, nitrogenous materials were largely basic in their residual effect on the soil. Mixtures made from such materials naturally also were basic. Increased use of ammonium sulfate gradually reduced the basicity of fertilizers and finally resulted in strongly acid-forming mixtures and brought about the practice of using basic materials to offset this acidic influence. The principal basic material so used is dolomitic limestone.

Ross and Mehring[36] report data covering the equivalent acidity or basicity of mixed fertilizers for the period of 1880 to 1934. These data are reproduced in part in Table 81.

Soluble Salt Concentration. Injury to germinating seed and to the roots of growing plants may result from improper placement of fertilizer or from the use of excessive quantities. Such injuries result largely from the high salt concentration in the soil solution produced by the soluble salts contained in the fertilizer mixtures.[32, 40]

TABLE 81. CHANGES IN THE RESIDUAL ACIDITY AND BASICITY OF MIXED FERTILIZER

	Calcium Carbonate Equivalent in Pounds per Ton	
Year	Acidity	Basicity
1880	--	40.8
1885	--	11.5
1890	--	16.1
1895	--	39.2
1900	--	38.8
1905	--	23.9
1907	14.8	--
1910	31.4	--
1915	22.0	--
1920	15.4	--
1921	28.8	--
1922	40.0	--
1923	41.8	--
1924	39.4	--
1925	70.3	--
1926	81.2	--
1927	127.4	--
1928	130.6	--
1929	124.2	--
1930	141.8	--
1931	146.9	--
1932	148.5	--
1934	105.0	--

Present-day mixed fertilizers contain relatively high concentrations of soluble salts, due principally to the use of large quantities of soluble nitrogen and potassium compounds. Some of these soluble salts are toxic to plants at relatively low concentrations while others are much less toxic and cause damage only in high concentrations.

The effect of the use of different fertilizers on the concentration of the soil solution was studied by White and Ross.[43] These workers reported in 1937 that changes in concentration of the soil solution as a result of the use of a number of different fertilizers varied greatly with the different soils but that relative effects of the different fertilizers were always the same. Superphosphate and free ammonia appear to have the least effects on the salt concentration in the soil solution, whereas sodium nitrate and low-grade potash salts have the greatest effects.

REACTIONS IN FERTILIZER MIXTURES

The production of mixed fertilizer brings together a great variety of materials. Chemical reactions between such materials play an important role in determining the chemical and physical properties of the finished product.

Some of the materials in the fertilizer mixture are acid in reaction, some are alkaline, and others are neutral salts. Superphosphate and monoammonium phosphate are examples of materials that act as acids; ammonia, calcium cyanamid, magnesium oxide, and limestone are alkaline; and ammonium nitrate, ammonium sulfate, and potassium chloride are neutral salts commonly used in large quantities.

The possibilities of chemical reactions in the fertilizer mixture between these and other materials are numerous, varied, and complex. They result principally from the use of ammoniating solutions and liming materials. Many of these reactions occur at ordinary temperatures, but it should be kept in mind that large quantities of heat are liberated as a reaction product and that a rise in temperature increases the rate of reaction and initiates other reactions that would not otherwise occur.

The more important reactions may, for the sake of convenience of discussion, be divided into three general classes.

Neutralization. Reactions of neutralization dominate the processes of chemical change in the fertilizer mixture. Chiefly responsible are superphosphate, an acidic material, and ammonia and dolomite, two basic materials.

The ammoniation of standard superphosphate, either as a separate material or as a part of the fertilizer mixture, results in a complicated series of chemical reactions, described by Keenen[13] in 1930 and since discussed by numerous other workers.[10, 14, 34, 42] As pictured by Keenen[13] the complete ammoniation of standard superphosphate may be represented by five principal reactions as follows:

1. $H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$
2. $CaH_4(PO_4)_2 + NH_3 \rightarrow CaHPO_4 + NH_4H_2PO_4$
3. $2CaHPO_4 + CaSO_4 + 2NH_3 \rightarrow Ca_3(PO_4)_2 + (NH_4)_2SO_4$
4. $NH_4H_2PO_4 + CaSO_4 + NH_3 \rightarrow CaHPO_4 + (NH_4)_2SO_4$
5. $CaH_4(PO_4)_2 + 2NH_3 \rightarrow CaHPO_4 + (NH_4)_2HPO_4$

Neutralization of free phosphoric acid (reaction 1) is followed by a reaction involving monocalcium phosphate and ammonia until 1 mol NH_3 per mol water-soluble P_2O_5 has been used up (reaction 2). Next come reactions 3 and 4, which probably proceed more or less simultaneously. Finally, under controlled conditions of low temperature and moisture content, it is possible to direct the reactions in such a way that diammonium phosphate is formed (reaction 5), although such an end-product does not represent a stable condition.

For the ammoniation of concentrated superphosphate in the absence of calcium sulfate, White, Hardesty and Ross[42] give four reactions as follows:

1. $H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$
2. $CaH_4(PO_4)_2 + NH_3 \rightarrow CaHPO_4 + NH_4H_2PO_4$
3. $NH_4H_2PO_4 + NH_3 \rightarrow (NH_4)_2HPO_4$
4. $3CaHPO_4 + 2NH_3 \rightarrow Ca_3(PO_4)_2 + (NH_4)_2HPO_4$

Reactions 1 and 2 are common to both standard and concentrated superphosphate. Ross[34] states that diammonium phosphate (reaction 3) is a normal and stable component of ammoniated concentrated superphosphate and that tricalcium phosphate (reaction 4) is not found unless ammonia additions exceed 10 per cent and the temperature rises above 80° C.

Relatively large quantities of liming materials such as dolomite, limestone, precipitated calcium carbonate, and hydrated lime are used as conditioning agents, as neutralizers of potential acidity, and as sources of plant nutrients in the preparation of mixed fertilizers. In addition, alkaline compounds often are introduced into the fertilizer mixture as a part of other materials—calcium cyanamid, for example. Dolomite predominates in importance among such materials.

MacIntire and co-workers[17, 18, 19] report that at ordinary temperatures the principal reaction is between monocalcium phosphate, the important acidic constituent of superphosphate, and dolomite and results in the formation of the diphosphates of calcium and magnesium. Neutralization of free phosphoric acid and the possibility of the formation of small amounts of tricalcium and trimagnesium phosphates also are involved in the reaction between dolomite and superphosphate in the fertilizer mixture in the absence of ammoniation.

1. $4H_3PO_4 + CaCO_3 \cdot MgCO_3 \rightarrow CaH_4(PO_4)_2 + MgH_4(PO_4)_2 + 2H_2O + 2CO_2$
2. $2CaH_4(PO_4)_2 + CaCO_3 \cdot MgCO_3 \rightarrow 3CaHPO_4 + MgHPO_4 + 2H_2O + 2CO_2$
3. $2CaHPO_4 + 2MgHPO_4 + CaCO_3 \cdot MgCO_3 \rightarrow Ca_3(PO_4)_2 + Mg_3(PO_4)_2 + 2H_2O + 2CO_2$

When high calcium limestone is substituted for dolomite, similar reactions occur except that there is greater danger of formation of tricalcium phosphate and loss of available phosphoric acid.

1. $2H_3PO_4 + CaCO_3 \rightarrow CaH_4(PO_4)_2 + H_2O + CO_2$
2. $CaH_4(PO_4)_2 + CaCO_3 \rightarrow 2CaHPO_4 + H_2O + CO_2$
3. $2CaHPO_4 + CaCO_3 \rightarrow Ca_3(PO_4)_2 + H_2O + CO_2$

According to the work of Beeson and Ross [5, 6] there are two prinicpal reactions in the fertilizer mixture between dolomite and monoammonium phosphate, the important acidic constituent of ammoniated superphosphate:

1. $3NH_4H_2PO_4 + CaCO_3 \cdot MgCO_3 \rightarrow$
$CaHPO_4 + MgNH_4PO_4 + (NH_4)_2HPO_4 + 2H_2O + 2CO_2$
2. $5NH_4H_2PO_4 + 3CaCO_3 \cdot MgCO_3 \rightarrow$
$Ca_3(PO_4)_2 + 3MgNH_4PO_4 + 2NH_3 + 6H_2O + 6CO_2$

Beeson and Ross [5, 6] state that reaction 2 takes place only after the temperature has risen to 90° C. On this basis no loss of ammonia and no tricalcium phosphate formation are to be expected under ordinary operating conditions.

Similar reactions for monoammonium phosphate and high calcium limestone are:

1. $2NH_4H_2PO_4 + CaCO_3 \rightarrow CaHPO_4 + (NH_4)_2HPO_4 + H_2O + CO_2$
2. $3NH_4H_2PO_4 + 3CaCO_3 \rightarrow$
$Ca_3(PO_4)_2 + (NH_4)_2HPO_4 + NH_3 + 3H_2O + 3CO_2$

In explanation of the above reactions it should be stated that when limestone is used the formation of tricalcium phosphate and the loss of ammonia are greatly influenced by the proportion of limestone to monoammonium phosphate. This is at variance with the situation found for dolomite where the amount of dolomite present in the mixture seems to have little effect on the course of the reaction.

In most fertilizer mixtures monoammonium phosphate is present in association with calcium sulfate. Under such conditions the reaction with dolomite follows a somewhat different course:

$4NH_4H_2PO_4 + 2CaCO_3 \cdot MgCO_3 + CaSO_4 \rightarrow$
$Ca_3(PO_4)_2 + 2MgNH_4PO_4 + (NH_4)_2SO_4 + 4H_2O + 4CO_2$

Diammonium phosphate is not usually found as a component of ordinary types of mixed fertilizers but may be found in some special grades. Beeson [4] reports the following reaction between diammonium phosphate and dolomite:

$5(NH_4)_2HPO_4 + 3CaCO_3 \cdot MgCO_3 \rightarrow$
$3MgNH_4PO_4 + Ca_3(PO_4)_2 + 7NH_3 + 6H_2O + 6CO_2$

Double Decomposition. Neutral salts having no common ions may react with each other to form a new pair of salts. Such reactions usually are reversible and the salts taking part are known as reciprocal salt pairs.

A good example of important reciprocal salt pairs in the fertilizer mixture is the monocalcium phosphate-ammonium sulfate and calcium sulfate-monoammonium phosphate combination. Merz and co-workers [60] have shown that calcium sulfate-monoammonium phosphate is the stable salt pair of this group and that the reaction goes as follows:

$$CaH_4(PO_4)_2 + (NH_4)_2SO_4 \rightarrow CaSO_4 + 2NH_4H_2PO_4$$

In the fertilizer mixture there exist possibilities of many other similar reactions that affect the chemical and physical properties of the finished product significantly. The production of hygroscopic salts as a result of a reaction between relatively nonhygroscopic compounds is an excellent example of such an influence and is illustrated in the following reaction:

$$2KNO_3 + (NH_4)_2SO_4 \rightarrow K_2SO_4 + 2NH_4NO_3$$

The course followed by double decomposition reactions between reciprocal salt pairs and the extent of such reactions are not definitely fixed in many cases but are influenced by conditions, such as concentration, temperature, pressure, moisture, reaction, and the presence of other materials. With this fact in mind, the following reactions are cited merely as examples of possibilities and with no attempt to indicate the extent to which each may be expected to develop or the direction it may be expected to follow:

1. $NH_4NO_3 + KCl = NH_4Cl + KNO_3$
2. $NH_4H_2PO_4 + KCl = KH_2PO_4 + NH_4Cl$
3. $NH_4H_2PO_4 + KNO_3 = KH_2PO_4 + NH_4NO_3$
4. $CaH_4(PO_4)_2 + 2KNO_3 = Ca(NO_3)_2 + K_2H_4(PO_4)_2$
5. $CaH_4(PO_4)_2 + 2NaNO_3 = Ca(NO_3)_2 + Na_2H_4(PO_4)_2$
6. $CaH_4(PO_4)_2 + 2NH_4NO_3 = Ca(NO_3)_2 + (NH_4)_2H_4(PO_4)_2$
7. $NaNO_3 + KCl = NaCl + KNO_3$
8. $(NH_4)_2SO_4 + 2KCl = 2NH_4Cl + K_2SO_4$

Hydration. Water is present in mixed fertilizer in two quite different forms:

1. "Free" water physically held as a surface film surrounding the solid particles that make up the mixture and in porous materials by capillary action.
2. "Bound" water present in chemical combination with other compounds.

Free moisture is introduced into the fertilizer mixture as a part of the materials used. Additional quantities are released as a result of chemical reactions that take place in the mixture. It is necessary for the initiation of chemical reactions and plays an important part in determining their course and extent.

At the same time the finished product must be relatively low in free water content so that it will be in good physical condition. Damp, sticky, gummy mixtures are impossible to handle in the drill.

An essential part of the curing process to which mixed fertilizers are subjected is a shift from free water to bound water. This means principally a change of free water to water of crystallization.

Many compounds formed as the products of chemical reactions in the fertilizer mixtures possess this power to change free water into water of crystallization. They act as powerful chemical drying agents and work to great advantage in developing fertilizers having a desirable physical condition.

Examples of salts that may act as chemical drying agents in the fertilizer mixture are indicated in the reactions that follow:

1. $CaH_4(PO_4)_2 + H_2O \rightarrow CaH_4(PO_4)_2 \cdot H_2O$
2. $CaHPO_4 + 2H_2O \rightarrow CaHPO_4 \cdot 2H_2O$
3. $Ca_3(PO_4)_2 + 2H_2O \rightarrow Ca_3(PO_4)_2 \cdot 2H_2O$
4. $MgH_4(PO_4)_2 + 2H_2O \rightarrow MgH_4(PO_4)_2 \cdot 2H_2O$
5. $MgHPO_4 + 3H_2O \rightarrow MgHPO_4 \cdot 3H_2O$
6. $MgHPO_4 + 7H_2O \rightarrow MgHPO_4 \cdot 7H_2O$
7. $Mg_3(PO_4)_2 + 4H_2O \rightarrow Mg_3(PO_4)_2 \cdot 4H_2O$
8. $Mg_3(PO_4)_2 + 8H_2O \rightarrow Mg_3(PO_4)_2 \cdot 8H_2O$
9. $MgNH_4PO_4 + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O$
10. $CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$

A study of the above reactions shows that the phosphates and calcium sulfate are the principal chemical drying agents in the fertilizer mixtures and that the magnesium phosphates are especially effective. It should not be concluded, however, that these hydrations necessarily all go to completion under ordinary conditions. This does not appear to be the normal situation. MacIntire and Shaw[18] found, for example, that the trihydrate of dimagnesium phosphate rather than the heptahydrate is the one normally found in the fertilizer mixture, and Sauchelli[37] states that calcium sulfate ordinarily occurs as the anhydrite or hemihydrate rather than as the dihydrate.

PLANT NUTRIENTS SUPPLIED IN MIXED FERTILIZERS

The plant nutrient elements of principal commercial importance in mixed fertilizers are nitrogen, phosphorus, and potassium. These primary nutrient elements commonly are expressed in terms of nitrogen (N), phosphoric acid (P_2O_5), and potash (K_2O).

Next in importance are the secondary elements—calcium, sulfur, and magnesium—and finally there are the minor elements—boron, copper, manganese, molybdenum, and zinc. The present trend is toward guaranteeing these secondary and minor elements in fertilizers in terms of the elements but this practice is by no means universally followed.

In accord with their relative importance, the plant nutrients most commonly guaranteed in fertilizers are nitrogen, phosphoric acid, and potash. Guarantees for other nutrients are not required in most states.

Guarantees for nitrogen, phosphoric acid, and potash, stated in that order, constitute the "grade" of the fertilizer. Thus a 4–12–8 fertilizer contains 4 pounds of nitrogen, 12 pounds of phosphoric acid and 8 pounds of potash in each 100 pounds of the mixture or 80 pounds of nitrogen, 240 pounds of phosphoric acid, and 160 pounds of potash per ton.

TABLE 82. CHANGES IN THE NITROGEN, PHOSPHORIC ACID AND POTASH CONTENT OF MIXED FERTILIZERS

Year	Total Nitrogen [N] %	Available Phosphoric Acid [P_2O_5] %	Soluble Potash [K_2O] %	Total %
1880	2.3	8.9	2.2	13.4
1890	2.3	9.2	2.4	13.9
1900	2.0	9.2	2.9	14.1
1910	2.2	9.0	3.7	14.9
1920	2.2	8.9	2.8	13.9
1925	2.6	9.3	4.1	16.0
1926	2.7	9.5	4.3	16.5
1927	2.8	9.4	4.4	16.6
1928	2.9	9.6	4.5	17.0
1929	3.1	9.8	4.6	17.5
1930	3.2	9.7	4.9	17.8
1931	3.3	9.6	5.0	17.9
1932	3.4	9.5	5.1	18.0
1933	3.5	9.3	5.2	18.0
1934	3.6	9.2	5.3	18.1
1935	3.6	9.1	5.4	18.3
1936	3.8	9.3	5.5	18.5

The average mixed fertilizer used in 1945 contained 3.90 per cent nitrogen, 10.30 per cent available phosphoric acid, and 7.50 per cent soluble potash. This compares with 2.40 per cent nitrogen, 9.10 per cent available phosphoric acid, and 2.00 per cent potash in 1880 and 2.50 per cent nitrogen, 9.40 per cent available phosphoric acid and 4.10 per cent soluble potash in 1925.

TABLE 83. CHANGES IN THE AVERAGE NITROGEN, PHOSPHORIC ACID AND POTASH CONTENT OF MIXED FERTILIZERS

Year	Total Nitrogen [N] %	Available Phosphoric Acid [P_2O_5] %	Soluble Potash [K_2O] %	Total %
1900	2.0	9.4	2.5	13.9
1910	2.1	9.3	3.4	14.8
1920	2.3	9.2	2.4	13.9
1930	3.1	9.8	5.0	17.9
1940	3.8	9.6	6.5	19.9
1945	3.9	10.3	7.5	21.7

Data covering changes in the nitrogen, phosphoric acid, and potash content of mixed fertilizers for the period of 1880 to 1936, as reported by Ross and Mehring,[36] are given in Table 82. Similar data reported by Jacob[11] for the period of 1900 to 1945 are given in Table 83.

Concentration of thought on the importance of nitrogen, phosphoric acid, and potash in mixed fertilizers has largely obscured the possible value of other plant nutrients. Evaluation of fertilizers on the basis of nitrogen, phosphoric acid, and potash content alone still persists to a large extent in spite of numerous investigations showing the importance of other plant nutrients added either accidentally as impurities or intentionally as special materials.[3, 21, 25, 85]

Considerable work now is in progress covering the detection of secondary and minor element deficiencies and their prevention and correction through the use of fertilizers.[20, 39, 41] Important items in such studies are the amounts of these plant nutrients needed in fertilizers and the need for their control, especially in high-analysis mixtures.

THE ECONOMY OF HIGH ANALYSIS

In the early days mixed fertilizers were made entirely from industrial by-products and waste-products and from materials mined from natural mineral deposits. All of these materials were relatively low in their content of the primary plant nutrients—nitrogen, phosphoric acid, and potash. So also, of necessity, were the mixtures made from them. During the first fifty years of the industry little opportunity was found for the preparation of higher-analysis mixtures.

New materials developed in recent years—synthetic nitrogen compounds, concentrated superphosphate, highly purified potash salts—have radically changed this picture. Mixed fertilizers no longer must be made up largely of low-grade organic by-products and waste materials but may be compounded from a wide choice of relatively concentrated and highly purified chemicals. These new materials have made possible the preparation of mixtures of greatly increased nitrogen, phosphoric acid, and potash content.

The economic advantages to be gained by increasing the nitrogen, phosphoric acid, and potash content of mixed fertilizers are easy to demonstrate and have been emphasized by numerous workers.[11, 33, 35, 39] Such increases mean lower costs for transportation, handling, storage, and bagging and thus make it possible to deliver the fertilizer on the farm at a lower cost per pound of these plant nutrients. This may be conveniently illustrated by comparing 4–8–8 and 5–10–10, two grades of mixed fertilizer having the same ratios of nitrogen, phosphoric acid, and potash.

Eight hundred pounds of 5–10–10 supplies the same quantity of these plant nutrients as does 1000 pounds of 4–8–8. The nitrogen, phosphoric acid, and potash is the same but the 5–10–10 is delivered to the farm cheaper because it requires less labor to produce, takes up less storage space in the factory, uses up a fewer number of bags, and needs fewer trucks or freight cars when it is shipped.

A good dividing line between low- and high-analysis fertilizers—between economical and too costly mixtures—will vary with the different grades and with the different formulas used but generally lies within the range of 20 to 30 per cent as the sum of the nitrogen, phosphoric acid, and potash content. Lower grades are uneconomical, often contain worthless filler and use up too much scarce material, such as labor, bags, and transportation. Much higher grades on the other hand necessitate the use of highly concentrated materials that usually are deficient in important secondary and minor plant nutrient elements and often are strongly acid-forming.[33]

Considerable progress already has been made toward increasing the nitrogen, phosphoric acid, and potash content of mixed fertilizers. It rose steadily, for example, from an average of 13.9 per cent in 1920 to more than 21 per cent in 1946. Much still remains to be done, however, for present materials make it easily possible to go higher with no possible lowering of quality and new materials and new processes promised for the future increase this possibility.

An important item in holding back progress toward more highly concentrated mixtures is the fact that farmers in many parts of the country have been slow to develop enthusiasm for them. Largely responsible for this hesitation are the facts that they have obtained good results from the use of the less concentrated fertilizers, are accustomed to using them, and own distributing machinery that is not always suited to the change. It also is true that the more highly concentrated fertilizers have not always given as good results as the more standard mixtures, especially when used on light sandy soils, due to their lower content of secondary and minor plant foods and higher residual acidity.

STATE CONTROL LAWS

The distribution of commercial fertilizer is regulated by state control laws. These laws cover both mixed fertilizers and materials distributed for use as such. They are designed to protect the purchaser by providing information needed to evaluate the quality of the fertilizer and by preventing the sale of inferior and harmful materials and mixtures.

The first effective fertilizer law was enacted in Massachusetts in 1873. Earlier laws enacted in Maryland, Massachusetts, North Carolina, and Virginia were ineffective in accomplishing their purpose due to the fact that they carried no provisions for the collection and analysis of samples by the state.

Today all states have fertilizer control laws. Many of these state laws have remained in effect with only minor amendments over a long period of years, whereas others have received major revisions or have been completely rewritten in recent years in recognition of the changing nature of the fertilizer control problem.

State control laws, as a general thing, provide for the registration of brands and grades, set up penalties for violations, require guarantees covering at least the primary plant nutrients—nitrogen, phosphoric acid, and potash—and provide for a system of inspection and analysis.

FIG. 25. An inspector prepares to take a sample as the first step in the operation of a State Fertilizer control Law that gives needed protection to both the farmer and fertilizer producer. (Courtesy South Carolina Agr. Expt. Sta.)

In some states guarantees for other plant nutrients are required or permitted, the minimum total of nitrogen, available phosphoric acid and potash that can be guaranteed is set up, and provision is made for limiting the grades of mixed fertilizer that can be sold. Other provisions prohibit the use of ingredients considered harmful, require a declaration regarding the residual acidity or basicity of the fertilizer, and necessitate guarantees covering materials used in compounding mixed fertilizers.

Methods of sampling and analysis used in state control work are, almost without exception, those adopted by the Association of Official Agricultural Chemists. These methods have been worked out and im

TABLE 84. CONSUMPTION AND NITROGEN, PHOSPHORIC ACID AND POTASH CONTENT OF MIXED FERTILIZER FOR THE YEAR ENDING JUNE 30, 1946

State and Region	Mixed Fertilizers tons	Nitrogen tons	Phosphoric Acid tons	Potash tons
Maine	245,260	14,914	23,978	32,080
New Hampshire	15,844	848	1,710	1,571
Vermont	18,682	946	2,350	2,146
Massachusetts	66,745	3,706	5,946	5,553
Rhode Island	14,079	710	1,420	1,307
Connecticut	56,149	3,234	4,438	4,364
New England	416,759	24,358	39,842	47,021
New York	386,992	17,694	43,532	28,356
New Jersey	222,752	9,852	25,351	19,128
Pennsylvania	424,998	15,307	52,710	31,278
Delaware	48,093	1,587	5,404	4,170
District of Columbia	1,113	54	122	67
Maryland	204,319	7,264	23,530	16,074
West Virginia	46,538	1,679	5,718	3,044
Middle Atlantic	1,334,805	53,437	156,367	102,117
Virginia	473,606	16,057	49,108	30,061
North Carolina	1,297,868	47,194	124,760	82,907
South Carolina	596,300	22,324	58,442	39,014
Georgia	822,873	31,315	74,210	51,119
Florida	814,960	35,207	56,033	58,066
South Atlantic	4,005,607	152,097	362,553	261,167
Ohio	642,856	14,969	80,318	49,119
Indiana	534,246	10,134	65,958	51,883
Illinois	195,232	4,192	23,559	20,006
Michigan	305,415	6,981	38,143	26,213
Wisconsin	226,850	4,810	29,216	24,421
East North Central	1,904,599	41,086	237,194	171,642
Minnesota	70,565	1,862	9,962	7,505
Iowa	100,980	2,159	13,222	8,792
Missouri	112,681	3,025	14,328	7,524
North Dakota	6,129	146	916	681
South Dakota	815	19	101	55
Nebraska	1,188	73	239	38
Kansas	11,476	322	1,498	649
West North Central	303,834	7,606	40,266	25,244
Kentucky	207,698	6,885	22,508	13,328
Tennessee	223,896	6,747	23,814	14,340
Alabama	524,789	24,456	51,441	30,084
Mississippi	242,578	12,791	21,514	14,986
Arkansas	97,413	4,408	10,115	7,550
Louisiana	132,711	5,883	14,736	6,854
Oklahoma	17,376	702	2,077	967
Texas	181,868	8,387	20,879	8,112
South Central	1,628,329	70,259	167,084	96,203
Montana	1,391	91	286	34
Idaho	5,952	459	771	126
Wyoming	263	26	51	10
Colorado	5,289	394	1,124	210
New Mexico	1,300	83	193	36
Arizona	10,688	1,095	2,097	35
Utah	1,755	119	330	65
Nevada	81	7	12	2
Washington	43,376	2,505	4,564	2,850
Oregon	27,337	1,566	3,229	1,787
California	271,677	21,220	24,960	16,386
Western	369,109	27,565	37,617	21,541
Hawaii	44,221	5,070	2,841	6,827
Puerto Rico	193,761	19,352	12,351	20,231
Alaska	220	12	22	20
Territories	238,202	24,434	15,214	27,078
Continental U.S.	9,963,042	376,408	1,040,923	724,935
Total	10,201,244	400,842	1,056,137	752,013

proved with great care and diligence and now have acquired a relatively high degree of perfection (Figure 25).

The principal weakness of fertilizer control laws at the present time is the lack of uniformity between states. Even adjoining states often have entirely different requirements that place an unnecessary burden on producers who sell fertilizer over a large territory. In view of this situation it is encouraging to note that a recent movement for greater uniformity is making rapid progress and promises an accomplishment of real merit.[9]

In practice, the operation of state fertilizer control laws has, as a whole, been efficient, fair, and satisfactory to all concerned with the production, distribution, and use of fertilizers. These laws provide needed protection to both the producer and the consumer and have been a potent factor in promoting progress in the manufacture and use of fertilizers.

CONSUMPTION

During recent years the United States Department of Agriculture has collected much valuable information regarding the use of fertilizers. This information usually has been released annually by Mehring and associates.[23, 24, 26, 27, 28, 29, 38]

Data taken from such U.S.D.A. releases form the basis for the following discussion which, for the sake of brevity, will be limited to the year ending June 30, 1946. This is the most recent annual period for which complete data are available and is a period typical of the postwar expanding fertilizer consumption.

Consumption of mixed fertilizers in the United States and its Territories during the year ending June 30, 1946, amounted to 10,201,244 tons. The corresponding value for 1945 is 9,065,775; for 1944, 8,639,682; and for 1943, 7,704,247.

A breakdown of this total consumption into states, territories, and regions is given by data presented in Table 84. Also given in table 84 are data presenting consumption in terms of actual nitrogen, phosphoric acid, and potash.

Mixed fertilizer consumption in North Carolina amounted to 1,297,868 tons. This placed North Carolina ahead of all other states, a position it has occupied for a number of years. Georgia was in second place with a consumption of 822,873 tons, Florida was in third place, and Ohio was fourth.

The heaviest consuming region was the South Atlantic, composed of the states of Virginia, North Carolina, South Carolina, Georgia and Florida. The 4,005,607 tons consumed here was more than double the amount used in any other region. The greatest rates of increases, however, are found in the East North Central, the West North Central, and the Western regions, where fertilizer use on a large scale is a more recent development.

The 10,201,244 tons given as the total consumption of mixed fertilizers contained 400,842 tons of nitrogen, 1,056,137 tons of phosphoric acid, and 752,013 tons of potash or a combined total of 2,208,992 for these three plant nutrients. These values represent 57 per cent of the nitrogen, 68 per cent of the phosphoric acid, 93 per cent of the potash, and 72 per cent of the combined nitrogen, phosphoric acid, and potash used in that year and indicate 3.9–10.4–7.4 as the average grade of mixed fertilizer used.

TABLE 85. PRINCIPAL FERTILIZER GRADES CONSUMED IN THE CONTINENTAL UNITED STATES, DURING YEAR ENDING JUNE 30, 1946

Grade	Consumption tons	Proportion of Total %
2-12-6	1,352,942	13.6
3-9-6	815,465	8.2
3-12-6	810,397	8.1
5-10-5	615,937	6.2
4-10-6	555,060	5.6
4-8-6	526,169	5.3
4-12-4	504,532	5.1
3-12-12	391,854	3.9
4-8-8	293,914	3.0
5-10-10	280,434	2.8
6-8-4	277,125	2.8
4-10-7	246,150	2.5
0-12-12	230,016	2.3
6-8-6	193,769	1.9
4-12-8	188,892	1.9
3-9-9	172,793	1.7
0-14-7	169,123	1.7
3-8-5	162,209	1.6
4-7-5	141,609	1.4
4-6-8	133,941	1.3
4-10-4	103,145	1.0
4-9-3	84,429	0.9
4-8-12	78,544	0.8
3-18-9	71,798	0.7
6-8-8	61,308	0.6
3-9-18	59,083	0.6
6-9-15	56,821	0.6
8-8-4	50,227	0.5
28 grades	8,627,686	86.6
278 other grades	1,335,356	13.4
Total, 306 grades	9,963,042	100.0

In contrast to the more than 1000 grades offered annually prior to 1940, a total of only 306 grades of mixed fertilizer was reported as sold in the continental United States during the year ending June 30, 1946. Even so, this represented an increase of 35 over the number sold during the preceding year.

The 28 most popular grades, together with the tonnage represented by each, are listed in Table 85. The 306 grades reported leave 238,202 tons of mixed fertilizer not accounted for out of the total of 10,201,244 tons.

The 2–12–6 grade, with a tonnage of 1,352,942, accounted for 13.6 per cent of all mixed fertilizer used and is far ahead of all others on the list. The 28 grades listed represented 86.6 per cent of the total tonnage. The remaining 13.4 per cent was divided between 278 other grades, no one of which represents more than a few thousand tons. Some of these grades were used over large territories while others were confined to use in a single state.

BIBLIOGRAPHY

1. Andrews, W. B., "The Response of Crops and Soils to Fertilizers and Manures." State College, Miss., W. B. Andrews (1947).
2. Bear, Firman E., "Soils and Fertilizers." 3rd ed. New York, John Wiley and Sons, Inc. (1942).
3. Bear, Firman E., *Am. Fertilizer* **108** (1): 9, 20, 22 (1948).
4. Beeson, Kenneth C., *Ind. Eng. Chem.* **29**: 705 (1937).
5. Beeson, Kenneth C., and Ross, W. H., *Ind. Eng. Chem.* **26**: 992 (1934).
6. Beeson, Kenneth C., and Ross, W. H., *Ind. Eng. Chem.* **29**: 1176 (1937).
7. Blair, A. W., *N. J. Agr. Expt. Sta. Bull.* **651** (1938).
8. Collings, Gilbeart H., "Commercial Fertilizers." 4th ed. Philadelphia, The Blakiston Co., Inc. (1947).
9. Coltrane, D. S., *Proc. Fertilizer Conference, U. S. D. A., Assoc. Am. Fert. Control Officials and Am. Soc. Agron.*, pp. 114–127 (1947).
10. Hardesty, John O., and Ross, W. H., *Ind. Eng. Chem.* **29**: 1283 (1937).
11. Jacob, K. D., *Am. Fertilizer* **107** (3): 7, 26, 28; **107** (4): 9, 26, 28, 30 (1947).
12. Jacob, K. D., and Mehring, A. L., *Agricultural Chemicals* **2** (12): 21, 61, 63, 65, 67 (1947).
13. Keenen, Frank G., *Ind. Eng. Chem.* **22**: 1378 (1930).
14. Keenen, Frank G., and Morgan, W. A., *Ind. Eng. Chem.* **29**: 197 (1937).
15. Lang, A. L., *Ill. Agr. Extension Service Release* **AG–1022** (1942).
16. Lundstrom, F. O., and Mehring, A. L., *Ind. Eng. Chem.* **31**: 354 (1939).
17. MacIntire, W. H., Hardin, L. J., and Oldham, F. D., *Ind. Eng. Chem.* **28**: 711 (1936).
18. MacIntire, W. H., and Shaw, W. M., *Ind. Eng. Chem.* **24**: 1401 (1932).
19. MacIntire, W. H., and Shuey, G. A., *Ind. Eng. Chem.* **24**: 933 (1932).
20. McMurtrey, J. E., Jr., *U. S. D. A. Tech. Bull.* **340** (1933).
21. McMurtrey, J. E., Jr., and Robinson, W. O., "Soils and Men." U.S.D.A., Yearbook of Agriculture, pp. 807–29. Washington, D. C., Govt. Printing Office (1938).
22. Mehring, A. L., *Am. Fertilizer* **106** (10): 7, 26, 28, 30 (1947).
23. Mehring, A. L., Bailey, E., and Wallace, H. M., *Natl. Fert. Assoc. 20th Ann. Conv. Proc.*, Sect. 2, 1944.
24. Mehring, A. L., Deming, L. S., and Willett, H., "A Survey of Plant-Food Consumption in the U. S. in the Year Ended June 30, 1939." Natl. Fert. Assoc., Washington, D. C. (1940).
25. Mehring, A. L., and Lundstrom, F. O., *Am. Fertilizer* **88** (2): 5 (1938).
26. Mehring, A. L., and Peterson, Avis J., *Com. Fert. Yearbook, 1934*, pp. 33–44.
27. Mehring, A. L., and Vincent, G. P., *U.S.D.A. Circ.* **689** (1943).

28. Mehring, A. L., Wallace, Hilda M., and Drain, Mildred, *U.S.D.A. Circ.* **756** (1946).
29. Mehring, A. L., Wallace, Hilda M., and Scholl, Walter, *Am. Fertilizer* **105** (4): 7, 26, 28, 30 (1946).
30. Merz, Albert R., Fry, William H., Hardesty, John O., and Adams, J. Richard, *Ind. Eng. Chem.* **25**: 136 (1933).
31. Moore, H. C., "Am. Fertilizer Handbook," Philadelphia, Pa., Ware Bros. Co., pp. 21–57 (1946).
32. Rader, L. F., White, L. M., and Whittaker, C. W., *Soil Sci.* **55**: 201 (1943).
33. Reed, J. F., and Alexander, L. T., *Am. Fertilizer* **106** (12): 9, 24, 26, 28 (1947).
34. Ross, William H., *Am. Fertilizer* **80** (4): 5, 6, 24, 26 (1934).
35. Ross, William H., and Beeson, Kenneth C., *Am. Fertilizer* **90** (5): 5, 24, 26; (6): 6, 8, 9 (1939).
36. Ross, William H., and Mehring, Arnon L., "Soils and Men." U. S. D. A., Yearbook of Agriculture, pp. 522–545. Washington, D. C., Govt. Printing Office (1938).
37. Sauchelli, Vincent, "Manual on Fertilizer Manufacture." Baltimore, Md., The Davidson Chemical Corporation (1946).
38. Scholl, Walter, Wallace, Hilda M., and Mehring, A. L., *U.S.D.A. Mimeo. Release* (1947).
39. Skinner, J. J., *Am. Fertilizer* **88** (13): 10, 24; **89** (3): 5, 22, 24, 26 (1938).
40. Skinner, J. J., Nelson, W. L., and Whittaker, C. W., *J. Am. Soc. Agron.* **37**: 677 (1945).
41. Volk, N. J., Tidmore, J. W., and Meadows, D. T., *Soil Sci.* **60**: 427 (1945).
42. White, Lawrence M., Hardesty, John O., and Ross, William H., *Ind. Eng. Chem.* **27**: 562 (1935).
43. White, L. M., and Ross, W. H., *J. Agr. Research* **59**: 81 (1939).

Chapter XI

LIMING MATERIALS

A. C. Richer

The Pennsylvania State College, State College, Pa.

The most important single factor limiting maximum crop production in Eastern United States is excessive soil acidity. Lime frequently has been referred to as the "backbone" of sound soil management practices since it not only supplies calcium and magnesium for plant growth but also creates a desirable physical, chemical, and biological soil environment for the growth of plants.

It has been estimated that approximately three-fourths of the cultivated land in the humid region of United States would be materially benefited by lime [48] even though the knowledge of the value of lime for soil improvement was brought to America by our colonists.[55] Except in a few localized areas however, liming was not practiced extensively in this early period until it became increasingly apparent, through the teachings of Ruffin,[38] in 1835, and later Wheeler,[52] Hilgard,[17] Hopkins,[18] Frear,[12] and others, that the intelligent use of agricultural liming materials was an essential part of sound soil management practices.

The use of liming materials has increased tremendously in the last few years by stimulus of the conservation program of the Agricultural Adjustment Administration, now the Production and Marketing Administration.[15] In 1925, just before the inception of the conservation program, the total amount of liming materials used by farmers in the United States was approximately 3½ million tons, whereas in 1947 almost 30 million tons were used. It has been estimated that about 50 million tons can be used profitably each year by the United States.

Development of Soil Acidity

Soil reaction refers to the condition of soils with respect to acidity or alkalinity. In the terminology of the farmer, "sour soils" are acid soils, whereas "sweet soils" implies neutral or alkaline soils adequately supplied with calcium and magnesium. Soils become acid as the amount of available calcium on the colloidal exchange complex is gradually depleted and replaced with exchangeable hydrogen. The losses of calcium and magnesium occur in the surface soils of the East in three ways—leaching, crop removal, and erosion. By far, the greatest losses occur through leaching.

Soils of Eastern United States are predominantly acid due to the continuous removal of calcium in drainage waters. A line drawn north-south along the 97th meridian divides the soils of United States approximately into acid soils and neutral or alkaline soils (Figure 26). Soils east of this so-called "lime-line" are exposed to over 25 inches of annual rainfall and thus suffer a loss of bases as calcium in excess of the amount replaced by normal weathering processes of soil minerals. Soils west of the lime-line, however, have insufficient rainfall to completely leach out the calcium and actually have layers of accumulation of $CaCO_3$ at various depths. These layers of accumulation are progressively nearer the surface as the amount of annual precipitation decreases. Thus, soil acidity is not a problem in Western United States except in certain areas along the Pacific Coast where the annual precipitation is again in excess of 25 inches per year.

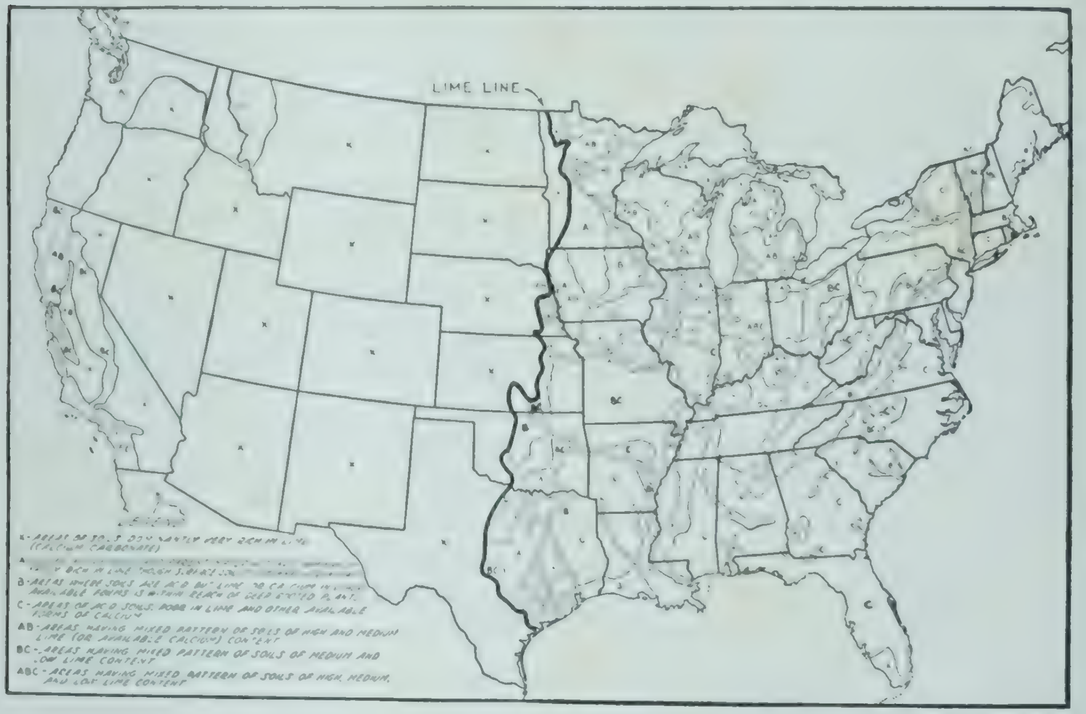

LIME LINE
X - AREAS OF SOILS DOMINANTLY VERY RICH IN LIME (CALCIUM CARBONATE)
B - AREAS WHERE SOILS ARE ACID BUT LIME OR CALCIUM IN AVAILABLE FORMS IS WITHIN REACH OF DEEP ROOTED PLANTS
C - AREAS OF ACID SOILS. POOR IN LIME AND OTHER AVAILABLE FORMS OF CALCIUM
AB - AREAS HAVING MIXED PATTERN OF SOILS OF HIGH AND MEDIUM LIME (OR AVAILABLE CALCIUM) CONTENT
BC - AREAS HAVING MIXED PATTERN OF SOILS OF MEDIUM AND LOW LIME CONTENT
ABC - AREAS HAVING MIXED PATTERN OF SOILS OF HIGH, MEDIUM, AND LOW LIME CONTENT

FIG. 26. The "lime line" and the relative contents of available calcium of the soils of the United States (Shorey [41]).

Lysimeter experiments at Cornell [8] have shown that the magnitude of this leaching loss is approximately 500 pounds of calcium and magnesium carbonate per acre. However, other experiments at Illinois [44] and Wisconsin [19] indicated that when natural surface drainage was permitted, the losses were much less because the excess water ran off and was not forced to percolate through the soil. On the basis of these latter experiments, Truog [18] estimated that the annual loss of lime carbonates by leaching was not more than 100 pounds per acre. In spite of this diversity of results, it is generally agreed that the primary cause of soil acidity of the humid region soils is the considerable loss of lime by leaching.

The rate of loss of lime is actually affected by several factors, notably (1) the amount of rainfall, (2) cropping system, (3) texture of the soil, and (4) amount and frequency of lime application. It is obvious that with increasing rainfall, the degree of leaching will be accentuated. Lysimeter experiments [23] have shown that losses are greatest on bare soils and that the magnitude of the loss is affected by the type of vegetation. Sandy soils with low base exchange capacities have little ability to retain calcium and thus yield any added calcium to percolating waters much more readily than clay soils. Losses are also less when small frequent applications of lime are made rather than single heavy applications.[27]

In addition to the losses by leaching, appreciable amounts of calcium may be removed or lost from the soil by crop removal and erosion.[23] The amounts removed by crops may vary from one to over 200 pounds of $CaCO_3$ per acre per year depending upon the crop, with the largest amounts removed by legumes.[57] The losses by erosion are extremely variable, depending upon the management and erodibility of the soils, but summaries by Lyon and Buchman [23] of the Missouri data indicate that the losses may be appreciable in certain instances.

The development of soil acidity is indirectly affected by other factors such as vegetation [27] and the use of certain fertilizers.[3] Coniferous trees particularly return very little calcium to the surface soil in the deposition and decay of their leaves. The very acid reaction of true podsolic soils is partially due to the coniferous vegetation on these soils. The continued use of certain nitrogenous fertilizers containing little or no basic constituents, such as ammonium sulfate, ammonium nitrate, urea, dried blood, anhydrous and aqua ammonia, will increase soil acidity. It should be noted, however, that commercial mixed fertilizers are usually prepared to be physiologically neutral and effect no change in soil acidity. (See Chapter X.) Furthermore, other fertilizers as calcium cyanamide and calcium nitrate leave an alkaline residue and thereby act partially as liming materials. (See Chapter VII.)

Two Types of Soil Acidity. With increasing losses of the basic ions, particularly calcium, soils become progressively more acid. The proportion of the hydrogen ions absorbed on the colloidal complexes increases, accompanied by a simultaneous increase in the hydrogen ion concentration of the soil solution, since both are in equilibrium.

Active acidity represents the number of the hydrogen ions in soil solution and is expressed by pH, while *exchange acidity* is a measure of the amount of hydrogen ions held in reserve exchangeable form on the colloidal complex. *Total acidity* is the sum of both active and exchange acidity but it is approximately equal to the exchange acidity since the total quantity of hydrogen ions in soil solution is only a minute portion of the total acidity. It has been estimated[3, 23] that 1 to 2.5 pounds of $CaCO_3$ would be sufficient to neutralize the active acidity of a soil with a pH 4, and yet several tons of limestone would be needed to raise the pH of the soil to pH 6.5. The exchange acidity acts as a weakly ionized acid buffer preventing any sharp rise in pH, and only when most of these hydrogen ions have been replaced by calcium or some other basic ions will the pH of the soil solution approach pH 6.5.

Sometimes, the question is raised, "If rain leaches out the bases such as calcium and magnesium, why aren't the acids leached out also?" It is obvious from the preceding statements that the "soil acids" are not water soluble since they are the clay and humus colloidal soil particles themselves more or less saturated with hydrogen. As a matter of fact, continued leaching will make the soil more acid. Ionization of carbonic acid in the soil solution supplies a continuous source of hydrogen ions which replace the calcium and other basic ions on the colloidal complex, and once these basic ions are in soil solution, they are susceptible to leaching losses.

EFFECT OF SOIL REACTION ON SOILS AND PLANTS

Effect of Hydrogen Ion Itself. It has been shown that the common agricultural plants are not adversely affected by the hydrogen ion itself in any normal pH range of soils of the humid region. The extreme acidity encountered in normal soils is about a pH of 4, and at this pH, if no other adverse factors are present, normal growth of many plants can be maintained.[4] As a matter of fact, the acidity of the sap of certain plants is in the range of our most acid soils.[46]

Effect on Calcium and Magnesium Supply. Calcium is an important essential element needed by all plants and used in particularly large amounts by legumes. It functions in regulatory processes as in regulating acidity in plants, permeability of membranes, cell wall construction, and translocation of carbohydrates and proteins, and on their storage during seed formation. Magnesium is an essential constituent of the chlorophyll molecule and is also related to the absorption and utilization of other plant nutrients such as phosphorus. Recently Albrecht[1] claimed that the main value of liming is that of adding calcium, rather than other effects. Although he obtained satisfactory results with a nonneutralizing source of calcium as gypsum, others[13, 34, 46] have not corroborated his findings. The differences of opinions and results may be due to the type of colloid present in the soils tested.[37] Undoubtedly one of the desirable effects of liming is to supply calcium and magnesium for plant growth, but it is generally accepted that secondary effects of liming in creating a desirable environment for the growth of plants are of considerable importance as well.

The importance of calcium in relation to the composition and nutritive value of plants has been described by Smith and Hester[43] and although there is some evidence on this point, further study is needed on this issue.

Effect on Other Elements. The effect of soil reaction on the availability of plant nutrients has been summarized by Truog[49] and is shown graphically in Figure 27. The maximum availability of most plant nutrients occurs at a pH of 6.5.

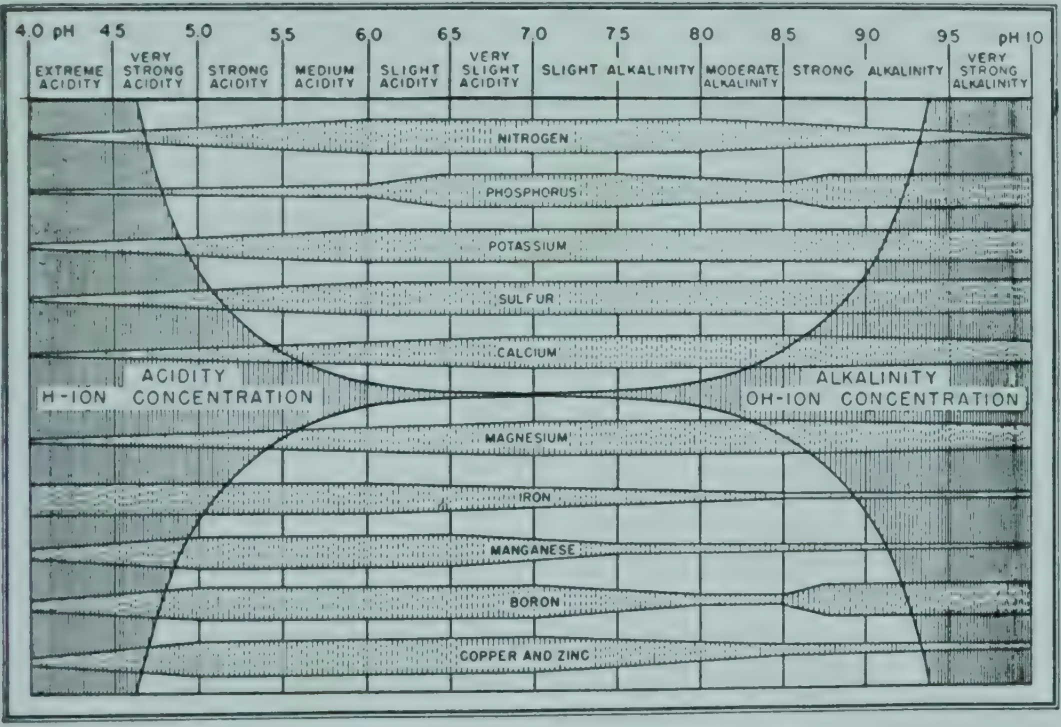


FIG. 27. The availability of plant nutrients in relation to soil reaction (Truog[49]).

As the pH decreases, the amounts of soluble iron, aluminum, and manganese increase, and at least one or more of those may be toxic to plant growth when present in large amounts. Manganese, particularly, is toxic in very acid soils.

Since the amount of soluble iron and aluminum increases with acidity, greater quantities of any available phosphorus are precipitated as iron and aluminum phosphates and gradually converted into unavailable basic forms.[50] The available phosphorus is almost invariably low in acid soils of Northeastern United States. In neutral or slightly acid soils, the calcium ion competes with the iron and aluminum and makes more of the phosphorus available by the formation of more soluble calcium salts. However, in alkaline or overlimed soils, the phosphorus will be precipitated as tricalcium phosphates,[35] which again are not as available as the di- and monocalcium phosphates found at a pH of 6 to 6.5.

In very acid soils, the amount of available potassium will usually be low since the colloidal complex will be saturated primarily with hydrogen. However, liming will not release additional soluble potassium but exerts a slight repressive effect upon the potassium solubility as shown by experiments at Tennessee.[25] It has also been established that calcium and potassium have an antagonistic effect regarding their absorption by plants. Thus with alfalfa, for example, if the calcium content of a soil is low, the plant will take up more potassium than it needs. Since calcium is less expensive than potassium, it is economically desirable to maintain an adequate supply of calcium in the soil.[7] Furthermore, the quality of the harvested crop is increased, since calcium is more important in the nutrition of animals than potassium.

TABLE 86. RELATIVE VALUE OF CROPS PER ROTATION PRODUCED BY COMMERCIAL FERTILIZERS (N–P–K) ON LIMED AND UNLIMED LAND. SUMMARY OF FOUR PENNSYLVANIA SOILS [54]

Nature of Soil	N-P-K Limed Land	N-P-K Unlimed Land	Increased Value on Limed Land	Per Cent Increase
Hagerstown soil	$156.81	$94.50	$62.31	65.9
Dekalb soil	100.81	41.47	59.34	143.1
Volusia soil	100.31	56.57	43.74	77.3
Westmoreland soil	124.00	68.49	55.51	81.1
General Average	120.48	65.26	55.22	84.7

In alkaline or overlimed soils, particularly sandy soils, deficiencies of trace elements as boron have been reported.[28, 31] This may be due not only to the actual depression of the quantity of boron in soil solution, although calcium and boron are antagonistic,[36] but also to a secondary effect that becomes apparent only when the limiting factor of soil acidity is removed. The soil may have been low in boron originally, and the deficiency becomes apparent only because of increased plant growth as a result of liming, and increased fixation in organic forms by stimulated microbiological activity. In addition to boron, there are indications that overliming may cause deficiencies of manganese, zinc, or copper[36, 40, 19] particularly on sandy soils.

Effect on Soil Microorganisms. The optimum reaction for most soil microbial activities is at or near neutrality. The ammonifying organisms are a diversified group and can function over a wide range of pH, but the optimum pH range for nitrification is 6–8. Cellulose is decomposed most rapidly at pH 7.3. Practically all of the important symbiotic nitrogen-fixing bacteria must have a pH at or near neutrality to function. Of the nonsymbiotic bacteria, *Azotobacter* will not survive in soils with a pH below 6, while *Clostridia* function in acid soils.

Effect on Efficiency of Fertilizers. White[54] and others[16] have demonstrated very strikingly that lime is absolutely essential for maximum returns from applied fertilizer on acid soils. Complete fertilizer on limed land produced a crop value of 84.7 per cent above that of the same fertilizer or unlimed land (Table 86). The relative value of lime for miscellaneous crops in terms of increases over unlimed land is shown in Table 87. Although alfalfa was not included in the list, the returns for alfalfa undoubtedly would be even greater than for mixed clover hay. Of the grain crops, barley responds the most to lime, whereas buckwheat responds the least.

TABLE 87. RELATIVE VALUE PER ACRE OF MISCELLANEOUS CROPS PRODUCED BY COMMERCIAL FERTILIZERS ON LIMED AND UNLIMED LAND. AVERAGE OF TWO PENNSYLVANIA SOILS [54]

Crops	N-P-K Limed Land	N-P-K Unlimed Land	Increase on Limed Land	Per Cent Increase
Mixed clover hay	$18.06	$ 4.18	$13.88	332.1
Barley	22.50	6.59	15.91	241.6
Clover and timothy hay	14.21	6.03	8.18	135.7
Kentucky bluegrass hay	10.06	4.25	5.81	136.7
Wheat	22.91	12.33	10.58	85.8
Corn for grain	23.62	12.75	10.87	85.3
Mixed pasture grass hay	16.45	9.38	7.07	75.4
Soybean hay	18.50	11.60	6.90	59.5
Ensilage corn	39.45	24.95	14.50	58.1
Timothy hay	12.16	7.97	4.19	52.6
Oats	23.07	16.55	6.52	39.4
Buckwheat	21.24	17.91	3.33	18.6
Average - Grain crops	22.67	13.22	9.45	71.5
Average - Forage crops	17.80	9.54	8.26	86.6
General average	20.23	11.38	8.85	77.8

Tolerance of Plants to Acidity. The fact that a plant survives under acid conditions does not necessarily indicate that it prefers acid soils but often means that the plant can tolerate such an environment and grows in spite of it. For example, sorrel is often used as an indicator plant of acid soils simply because it is acid tolerant, but sorrel will grow more luxuriantly on limed soil if it is not forced to compete with other plants. However, some plants, as the Ericaceous group, do best on acid soils, probably because of their high requirements of certain elements like iron. A list of the soil reaction preference of plants is shown in Table 88.

Effect on Soil Structure. Although calcium does not in itself create a desirable structure, it will tend to flocculate soil colloids and in that sense initiate the first phase of creating a desirable structure particularly where the colloids have been previously dispersed by excessive amounts of sodium in the soil. Indirectly, calcium helps to create and maintain a desirable soil structure of cropped soils by increasing crop yields and thereby increasing the amount of crop residues returned to the soil. Increased returns of organic matter to the soil through crop residues results in better structure, since organic matter is the most important single factor in creating good tilth. Calcium is also needed in larger quantities by the tap rooted legumes which open up compacted layers by root penetration.

DEFINITION OF TERMS RELATING TO LIMING MATERIALS

In the agricultural sense, the term "lime" refers to any compounds of calcium, or calcium and magnesium, which are capable of neutralizing

TABLE 88. SOIL REACTION PREFERENCES OF PLANTS. The plants listed will grow fairly well at least one-half pH unit below and above the optimum ranges given. Furthermore an asterisk at a pH value signified that fairly good growth of the plant concerned is common one full pH unit beyond the range thus marked (Truog, Graul, and Muckenhirn[50])

Common Name	Optimum pH Range	Common Name	Optimum pH Range
Legumes, Field and Garden		Cereals	
Alfalfa	6.5-8.0	Barley	* 6.5-8.0
Bean, White Navy	* 6.0-7.5	Buckwheat	* 5.5-7.0 *
Bean, Lima	* 6.0-7.0 *	Corn	5.5-7.0 *
Bean, Snap and Wax	* 6.0-7.5	Oats	5.5-7.0 *
Bean, Velvet	* 6.0-7.0	Rice	5.5-6.5
Clover, Alsike	5.5-7.5	Rye	5.0-7.0 *
Clover, Bur	5.0-6.5	Wheat	* 6.0-8.0
Clover, Crimson	5.5-7.0 *	Miscellaneous Field Crops	
Clover, Japan	5.5-6.5 *	Beet Mangel wurzel	6.0-7.5
Clover, Ladino	6.0-7.5	Beet Sugar	6.5-8.0
Clover, Mam. Red	6.0-7.5	Broom Corn	5.0-6.5 *
Clover, Sweet White	6.5-8.0	Cotton, Upland	5.0-7.0 *
Clover, Sweet Yellow	6.5-8.0	Flax	6.0-7.5
Clover, Red	6.0-7.5	Hemp	* 6.0-7.0 *
Clover, White	6.0-7.5	Potato	5.0-6.5 *
Cowpea	5.5-7.0	Potato, Sweet	5.5-6.5 *
Lespedeza, Jap.	5.5-7.0	Rutabaga	5.5-7.0
Lespedeza, Kor.	5.5-7.0	Sugar Cane	6.0-8.0
Lupine, Blue	5.0-6.5	Sunflower	* 6.0-7.5
Lupine, White	5.5-7.0	Tobacco	5.5-7.5
Pea, Canning and Garden	6.0-7.5	Turnip	* 6.0-7.0 *
Peanut	* 6.0-7.0 *	Rape	6.0-7.5
Serradella	* 6.0-7.0 *	Hay, Forage, and Pasture Grasses	
Soybean	* 6.0-7.0 *	Bermuda Grass	* 6.0-7.0 *
Vetch, Hairy	5.5-7.0	Bluegrass, Canada	* 6.0-7.5
Lupine, Yellow	5.0-6.0	Bluegrass, Kentucky	6.0-7.5 *
Tree and Tropical Fruits, Nuts and Berries		Brome Grass, Awnless	6.0-8.0
Apple	5.5-7.0	Fescue, Chewings	* 5.5-8.5 *
Apricot, Siberian	6.0-7.0	Fescue, Fine-leaves	* 6.5-7.5
Cherry, Sour and Sweet	6.0-7.5	Fescue, Meadow	5.0-7.0
Coffee	4.0-5.0	Fescue, Sheep's	5.0-6.5 *
Lemon	6.0-7.5	Italian Rye Grass	6.0-7.0 *
Grapefruit	6.0-7.5	Johnson Grass	5.0-6.0 *
Orange, Sweet	6.0-7.5	Meadow Fox-tail	6.0-7.5
Peach	6.0-7.5	Orchard Grass	6.0-7.0 *
Pear	6.0-7.5	Kafir Corn	6.0-7.5
Pecan	6.4-8.0	Millet	5.5-7.0 *
Pineapple	5.0-6.0	Milo, Dwarf Yellow	5.5-7.5
Plum, America	* 6.0-8.0	Redtop	* 6.0-7.0 *
Small Fruits		Reed's Canary Grass	6.0-7.0
Blackberry	5.5-7.0	Sudan Grass	5.5-7.0 *
Blueberry	4.5-5.8	Timothy	5.5-7.5 *
Cranberry, Large	4.3-5.3	Garden Crops	
Currant, Black and Red	5.5-7.5	Asparagus	6.0-8.0
Dewberry	4.5-6.0	Beet [Table]	6.0-7.5
Gooseberry, American	5.5-7.0	Broccoli	6.0-7.0
Grapes, many varieties	* 6.0-7.5 *	Brussels Sprouts	6.0-7.5
Raspberry, Black and Red	5.5-7.0	Cabbage	6.0-7.5
Strawberry	5.0-6.5	Cantaloupe	6.0-7.5

TABLE 88—CONTINUED

Garden Crops Cont.		Trees in General	
Carrot, Garden	5.5-7.0	Ash, White	6.0-7.5
Cauliflower	6.0-7.5	Aspen, American	5.0-6.5 *
Celery	6.0-7.5	Beech	5.0-6.7
Cucumber	5.5-7.0	Birch, Paper	5.0-6.5
Eggplant	5.5-6.0	Birch, Yellow	5.0-5.5
Endive	* 6.0-7.0	Catalpa, Western	6.0-8.0
Horseradish	5.5-7.0	Ceder, Red	5.0-8.0
Kale	6.0-7.5	Cottonwood	* 6.0-7.5 *
Kohl-Rabi	6.0-7.5	Chestnut, American	5.0-6.5
Lettuce	6.0-7.5	Elm, American White	5.5-8.0
Mushroom	6.5-7.5	Fir, Balsam	5.0-6.0
Onion	6.0-7.5	Fir, Douglas	6.0-7.0
Paprika, Red Pepper	6.5-8.0	Hemlock	5.0-5.5
Parsley	5.5-7.5	Hickory, Shagbark	6.0-7.5
Parsnip	5.5-7.5	Larch, European	6.0-8.0
Pepper	5.5-7.0 *	Locust, Black	6.0-7.5
Pumpkin	5.5-7.5	Maple, Sugar	5.5-7.0 *
Radish	6.0-7.5	Mulberry	6.5-7.5
Rhubarb	* 6.0-7.0 *	Oak, Black	5.5-6.5
Spinach	6.0-7.5	Oak, Bur	5.5-7.5
Squash, Hubbarb	5.5-7.5	Oak, Pin	5.0-6.5
Tomato	5.5-7.5	Oak, Red	* 5.5-6.5
Watermelon	5.5-6.5	Oak, White	6.0-7.5
Weeds		Pine, Jack	* 5.0-6.5
Bindweed, Field	6.0-7.5	Pine, Long leaf	4.0-6.0
Dandelion	5.5-7.0	Pine, Red	5.0-6.0
Dodder, Field	5.5-7.0	Pine, Western Yellow	5.5-7.5
Ivy, Poison	5.0-6.5	Pine, White	5.0-6.5 *
Lamb's Quarters	5.0-7.5	Pine, Short Leaf	5.0-6.0
Mustard, Wild	6.0-8.0	Poplar, Silver	6.0-8.0
Plantain, Common	6.0-7.5	Spruce, Black	4.5-5.0 *
Quack Grass	5.5-6.5	Spruce, Red	5.0-6.0
Sorrel, Sheep	5.5-7.0	Spruce, White	5.0-6.0
Thistle, Canada	5.0-7.5	Sycamore	6.0-7.5
Thistle, Russian	6.5-8.0	Tamarack	4.5-5.5 *
Thistle, Sow	6.0-7.5	Tung-oil Tree	5.0-6.0
		Walnut, Black	6.0-7.5
		Willow, Weeping	5.5-7.0
Ornamental Plants: Flowers, Shrubs & Vines			
Arborvitae, American	6.5-8.0	Ivy, English	6.0-8.0
Azaleas	5.5-7.0	Iris, Japanese	5.0-6.5
Begonias	5.0-7.0 *	Iris, Vernal	4.0-5.0
Calendula	6.0-7.5 *	Laurel, Great	4.5-6.0
Carnation	* 6.0-7.5 *	Lilac, common	6.0-7.5
Chrysanthemum	5.5-7.0 *	Lily, Easter	6.0-7.0
Cinerarias	5.0-6.5	Lily, Tiger	6.0-7.0
Clematic, Curly	5.5-7.0	Magnolia, Umbrella	5.0-6.0
Columbines	* 6.0-7.0	Mayflower	6.0-7.0
Cyclamens	5.0-6.5	Morning Glory	6.0-7.5
Dahlias	* 6.0-7.5	Narcissus, Polyanthus	6.0-7.5
Delphinium	6.0-7.5	Orchids	4.5-5.5
Eucalyptus	6.0-8.0	Pansy, Heart's Ease	5.5-6.5
Fern, Boston	5.0-6.5	Peony	6.0-7.5
Fern, Xmas	6.0-7.5	Phlox	5.0-6.0
Fern, Cliff	6.5-8.0	Pitcher plants	4.5-5.5
Fern, Cliff	6.5-8.0	Poinsettia	6.0-7.5
Fern, Cliff	5.0-6.0	Primrose	6.0-8.0
Fuchsias	5.5-6.5	Rhododendron	4.5-6.0
Gardenia	5.0-6.0	Roses	6.0-7.5
Geranium	6.5-8.0	Spierea	6.0-7.5
Gladiolus	6.0-7.5	Trailing Arbutus	4.5-6.0
Holly, American	5.0-6.0	Tulip, Common	6.0-7.0
Hydrangea	4.5-6.5	Wistaria	6.0-8.0
Iris	5.0-6.5	Zinnia	6.0-7.5

soil acidity. In a strict chemical sense, lime refers only to calcium and magnesium oxides, but agriculturally the term "liming material" is used loosely to include several compounds as carbonates, hydroxides, oxides, and sometimes silicates of calcium and magnesium.

The following definitions of terms relating to liming materials are those adopted by the Association of Official Agricultural Chemists[5] as of March, 1944.

Lime. The word *lime* when applied to liming materials means either calcium oxide or calcium and magnesium oxides. Interpretation—The term "lime" shall not be used in the registration, labeling, or guaranteeing of fertilizers or fertilizer materials unless the lime is in a form, or forms, to neutralize soil acidity.

Quicklime, burned lime, caustic lime, lump lime, unslaked lime. These designations shall apply to calcined materials, the major part of which is calcium oxide, in natural association with a lesser amount of magnesium oxide, and which is capable of slaking with water.

Hydrated or slaked lime is a dry product consisting chiefly of the hydroxide of calcium and oxide-hydroxide of magnesium.

Waste lime, by-product lime is any industrial waste or by-product containing calcium, or calcium and magnesium in forms that will neutralize acids. It may be designated by prefixing the name of the industry or process by which it is produced; i.e., *gas-house lime, tanners' lime, actelyene lime-waste, lime-kiln ashes, calcium silicate,* etc.

Gypsum, land plaster, or crude calcium sulfate are products consisting chiefly of calcium sulfate. They may contain 20 per cent of combined water. (They do not neutralize acid soils.)

High-Calcic products are materials in which 90 per cent or more of the total calcium and magnesium oxide content consists of calcium oxide.

High-Magnesic products are materials in which more than 10 per cent of the total calcium and magnesium oxide content consists of magnesium oxide.

Air-Slaked lime is a product composed of varying proportions of the oxide, hydroxide, and carbonate of calcium, or of calcium and magnesium, and derived from exposure of quicklime.

Pulverized limestone (fine ground limestone) is the product obtained by grinding either calcitic or dolomitic limestone so that all the material will pass a 20-mesh sieve and at least 75 per cent will pass a 100-mesh sieve.

Ground limestone (coarse-ground limestone) is the product obtained by grinding either calcitic or dolomitic limestone so that all the material will pass a 10-mesh sieve, and at least 50 per cent will pass a 100-mesh sieve.

Ground shells is the product obtained by grinding the shells of mollusks so that not less than 50 per cent will pass a 100-mesh sieve. The product shall also carry the name of the mollusk from which said product is made.

Ground shell marl is the product obtained by grinding natural deposits of shell marl so that at least 75 per cent will pass a 100-mesh sieve.

"Basic" lime phosphate (lime-based superphosphate) is a superphosphate to which liming materials have been added in a quantity at least 6 per cent calcium carbonate equivalents in excess of the quantity required to convert all water-soluble phosphate to the citrate-soluble form.

Dolomite is a mineral composed chiefly of carbonates of magnesium and calcium in substantially unimolal (1:1.19) proportions.

Magnesia (magnesium oxide) is a product consisting chiefly of the oxide of magnesium. Its grade shall be stipulated. For example: Magnesia—75 per cent MgO. (Proposed definition.)

Liming Materials

The most common agricultural liming materials are ground limestone, burned lime, and hydrated lime. The chemical relationship of these three is shown in the equation:

$$\underset{\text{(limestone)}}{CaCO_3} \xrightarrow{-\,CO_2} \underset{\text{(burned lime)}}{CaO} \xrightarrow{+\,H_2O} \underset{\text{(hydrated lime)}}{Ca(OH)_2}$$

Until 1909, practically all of the lime applied was in the form of burned lime, at which time pulverized limestone became a competitor on the agricultural lime market.[55] At the present time, however, of the three forms of liming materials, ground limestone is used to a much greater extent than all other forms combined.

In addition to limestone, other carbonates of calcium are used as liming materials, such as marl, oyster shells, and precipitated carbonates from various industries. For the farms near steel mills, blast furnace slag, which is partially a calcium silicate, has been found to be a cheap effective liming material also.

Ground Limestone. Limestone is a consolidated sedimentary rock composed of calcium and magnesium carbonates with varying amounts of impurities. Extensive deposits of limestone are found in many eastern states, and it is estimated that the supplies of raw limestone are inexhaustible. The purity may vary from 75 to 99 per cent calcium and magnesium carbonates, but commercial available limestones as a rule will analyze over 90 per cent carbonates. The commercial product is sold in paper bags or in bulk for farm use.

In some areas, limestone containing less than 90 per cent calcium and magnesium carbonates is pulverized for use on local farms, but any stone with less than 80 per cent carbonates should be considered a low-grade stone. In addition, these low-grade stones have other disadvantages, as difficulty in grinding if the diluting impurity is hard, as well as increased cost of transportation of inert material. Furthermore, when low grade stones are burned, the product will not slake readily.

Two general classes of limestones are available on the market: (1) high calcium limestones, (2) high magnesium limestones, often referred to as dolomitic limestones. According to the A.O.A.C. definitions, any stone with more than 10 per cent magnesium oxide (equivalent to approximately 21 per cent magnesium carbonate) is considered a high magnesium limestone. In industry, however, a stone with more than 10 per cent magnesium carbonate is referred to as a high magnesium limestone or dolomite.[15]

Limestone is available in several commercial grades of fineness, agricultural ground limestone, pulverized limestone, agricultural limestone meal, and limestone screenings. Of these, the one primarily prepared and sold for agricultural purposes is agricultural ground limestone. The pulverized limestone is appreciably finer than the ground limestone and is used especially for industrial purposes, while the agricultural ground limestone is not only cheaper, but just as satisfactory for agricultural purposes. The limestone screenings and limestone meal are rather coarse, passing approximately 4 and 8 mesh screens respectively, and are not used to any great extent except in localized areas.

The agricultural ground limestone, according to A.O.A.C. definitions, should all pass through a 10-mesh sieve, and at least 50 per cent of it through a 100-mesh sieve. Actually, much of the commercial agricultural ground limestone is prepared to have all of it pass a 20-mesh sieve and all of the finer material incidental to grinding retained, which usually results in a product that contains over 60 per cent through a 60-mesh sieve. In some states, this percentage through a 60-mesh sieve is also reported as part of the limestone fineness guarantee.

Oxides of Lime. When limestone is heated to a temperature of over 800° C., the calcium and magnesium carbonates decompose, yielding the respective calcium and magnesium oxides as shown by the equation:

$$\underset{100}{CaCO_3} \xrightarrow[800^\circ\text{ C.}]{\text{Heat}} \underset{56}{CaO} + \underset{44}{CO_2}$$

For every 100 pounds of calcium carbonate burned, 56 pounds of calcium oxide are formed. In an analogous fashion, for every 84.3 pounds of magnesium carbonates burned, 40.3 pounds of magnesium oxide are formed.

Commercially, the oxides of lime are produced by heating limestone in a kiln or oven with coal or gas as the source of heat. The oxides of lime formed are commonly referred to as "burned lime," or "quick lime," and in the lump condition as they come from the kiln, as "lump lime." A small amount of burned lime * is sold in the lump form, but most of it is ground to a fine white powder and sold in watertight paper bags. The lump lime should not be applied to the soil in the lump form since it cannot be incorporated thoroughly into the soil. For best results, the lump lime should be either ground or slaked before using for agricultural purposes.

Burned lime is a disagreeable material to handle in spreading on the soil because of its caustic effects on skin and eyes. It also presents a fire hazard due to its high affinity for water and simultaneous rapid release of heat. However, burned lime, as well as hydrated lime, neutralizes soil acidity more rapidly than limestone and is often preferred where rapid action is desired.

The purity of commercial burned lime depends upon the completeness of burning and the amount of impurity originally present in the limestone from which it was made. Commercial grades usually contain over 80 per cent combined calcium and magnesium oxides.

Hydroxides of Lime. On addition of water to calcium and magnesium oxides, the respective hydroxides are formed. The product is commonly called "hydrated" or "slaked" lime. In the strict chemical sense, the hydroxides of lime are not hydrates, but hydroxides formed from the respective anhydrides, as shown in the equation:

$$\underset{56}{CaO} + \underset{18}{H_2O} \longrightarrow \underset{74}{Ca(OH)_2}$$

For every 56 pounds of calcium oxide, 18 pounds of water are needed for proper "slaking," yielding 74 pounds of hydrated lime.** During this slaking process, considerable heat is evolved accompanied by a rapid increase in volume of the material with disintegration of the lumps of burned lime into a fine powder of hydrated lime.

The commercial product usually contains over 90 per cent combined calcium and magnesium hydroxides equivalent to from 65 to 73 per cent total calcium and magnesium oxides. As noted earlier, hydrated lime acts more rapidly in the soil than limestone, but it also possesses the same disagreeable caustic characteristics of burned lime.

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* In this discussion, the oxides of lime hereafter will be referred to as "burned lime," the most commonly used term.

** The hydroxides of lime hereafter will be referred to as "hydrated lime," the most commonly used term.

Limestone is still burned and slaked on many farms where the raw stone and fuel are readily available. If the piles of burned lime are not deliberately slaked, and simply exposed to the weather, a product known as "air-slaked lime" is formed. The exposed oxides gradually absorb water and carbon dioxide from the air, producing a variable mixture of oxides, hydroxides, and carbonates in the final product.

EVALUATION OF LIMING MATERIALS

The two most important factors which determine the desirability of any liming material are chemical composition and degree of fineness. It is a sound practice to evaluate all liming materials on the basis of these two factors—often referred to as the "chemical guarantee" and "fineness guarantee." As a matter of fact, a chart has been prepared by Schollenberger and Salter[39] which graphically estimates the value of a limestone of known fineness and chemical composition. However, for our purposes, it is sufficient to recognize and discuss briefly the significance of these two factors.

Chemical Guarantee. The total capacity of a liming material such as limestone to neutralize soil acidity is determined by its contents of calcium and magnesium compounds. The chemical guarantee may be expressed in various ways, as shown in Table 89. Of these, the conventional oxide content or the total lime oxides is usually the most accurate means of comparing miscellaneous liming materials. The calcium oxide equivalent is obtained by converting the magnesium oxide content to equivalent calcium oxide and reporting the sum of the two. Since magnesium has a lower atomic weight than calcium the calcium oxide equivalent gives additional value to limestones containing magnesium. The neutralizing power expresses the calcium and magnesium compounds in a liming material in terms of equivalent calcium carbonate. It should be noted that the calcium carbonate equivalent also gives additional value to liming materials containing magnesium. This is shown in Table 90 which compares the neutralizing values and the chemical equivalents of the pertinent pure calcium and magnesium compounds.

TABLE 89. VARIOUS EXPRESSIONS OF CHEMICAL GUARANTEES OF A REPRESENTATIVE LIMESTONE

Individual Carbonates	Total Carbonates	$CaCO_3$ Equivalent [neutralizing power]	Conventional Oxides	Total Lime Oxides	CaO Equivalent
$CaCO_3$ - 90% $MgCO_3$ - 5%	95.0%	95.93	50.40% 2.39%	52.79%	53.72

Because of the variations in presenting the chemical guarantees, considerable controversy and confusion exist regarding the best method of reporting these analyses. For simplicity, it is suggested that the analyses of the three common liming materials be reported on the basis of calcium and magnesium oxide content. In addition to uniformity, this single chemical guarantee is applicable to all three products and immediately indicates their relative abilities to neutralize soil acidity. The additional analyses now shown in chemical guarantees provide little, if any, useful supplemental information. With fertilizers, the guaranteed analyses are reported simply as percentages of N, P_2O_5, and K_2O, and comparisons of various fertilizers can be made directly with no confusion. A similar single chemical guarantee for liming materials would be desirable.

TABLE 90. NEUTRALIZING POWER AND CHEMICAL EQUIVALENTS TO CALCIUM CARBONATE OF LIMING MATERIALS

	Neutralizing Value or $CaCO_3$ Equivalent	Pounds Equivalent to One ton of Pure $CaCO_3$
$CaCO_3$	100	2000
$MgCO_3$	119	1680
$Ca[OH]_2$	135	1480
$Mg[OH]_2$	172	1160
CaO	178	1120
MgO	250	800

It is also suggested that the sum of the two oxides is a satisfactory basis for evaluating a liming material, rather than the calcium oxide equivalent. Thus, a good grade of limestone should contain 50 per cent or more lime oxides to be acceptable. In calculating the calcium oxide equivalent, slightly greater value is given to the per cent magnesium oxide. Whether liming materials should be credited with greater neutralizing value for the magnesium they contain is a disputed question. Results at Rhode Island[32] show that high calcium, and high magnesium liming materials when applied in chemically equivalent amounts gave approximately equal results, thereby indicating that magnesium should be credited with its additional neutralizing capacity. Greenhouse experiments at Pennsylvania[53] and field experiments at New Jersey,[21] however, indicated that calcium and magnesium limestones, when applied in equal weight amounts (not chemically equivalent amounts), produced yields of crops that were quite similar, indicating thereby that no additional credit should be ascribed to magnesium. Magnesium carbonate is less soluble than calcium carbonate[53] although it does have a slightly greater neutralizing value chemically. Therefore, from the practical viewpoint, both the calcium and magnesium carbonates can be considered on an equal basis. High magnesium limestone should be applied, however, on soil where there is any suspicion of magnesium deficiency.

Fineness Guarantee. White[53, 56] has shown conclusively that the effectiveness of limestone as a neutralizing agent of soil acidity is dependent upon the size of limestone particles, other factors being equal (Table 91). With increased fineness, the amount of surface exposed is greatly increased, and the solubility is affected accordingly. This is no problem with hydrated lime or ground burned lime, since the products are usually very fine powders; but with limestone, it is an essential evaluating factor. With finer limestones, more uniform distribution and intimate contact with soil particles are obtained. All of the limestone passing a 100-mesh sieve is available immediately, whereas the 60-mesh material becomes available during the first year after application. The stone between 20 and 60 mesh will require several years to dissolve.

TABLE 91. EFFECT OF FINENESS OF LIMESTONE PARTICLES ON THEIR DESIRABILITY AS LIMING MATERIALS[53]

Fineness	100 Mesh	60 Mesh	20 Mesh	8 Mesh
Solubility in carbonated water	100	57	45	28
Value in correcting acidity	100	57	27	18
Growth of plants	100	69	22	5

However, the finer a stone is ground, the greater is the cost to farmer, and the greater is the leaching loss of calcium from the soil. Some coarser particles are desirable to produce a lasting effect of the liming material.[14, 53] A limestone of intermediate fineness is recommended, such as one where all of the stone passes a 10- or 20-mesh sieve with about 40 or 50 per cent through a 100-mesh sieve.

Again, no uniform regulation exists. In some instances, it was required that a stone be ground so that all of it passes a 10-mesh sieve, and all of the incidental finer material created in pulverizing the stone be retained. Policing of such a requirement is almost impossible since unscrupulous manufacturers could screen out part of the more expensive finer material and still apparently meet the requirement.

Thus, for uniformity and ease in policing, it is suggested that a uniform requirement for agricultural ground limestone be adopted such as 100 per cent through a 20-mesh sieve, and 40 per cent through a 100-mesh sieve. Actually many manufacturers meet this requirement at present, so that little or no change would be required in the products now available.

COMPARISON OF THE THREE COMMON LIMING MATERIALS

When burned lime is incorporated into the soil, it is almost immediately converted to hydrated lime by its reaction with soil water. Chemically equivalent amounts of burned lime and hydrated lime act with the same speed and have the same total capacity of neutralizing soil acids. Limestone acts more slowly, the rate being determined by the fineness of the stone and also by the magnesium content. Over several years, however, the effect of agricultural ground limestone is the same as hydrated lime or burned lime when applied in equivalent amounts. This is to be expected since burned lime and hydrated lime are gradually converted to the carbonate forms in the soil. The primary difference between these three is spread of action.

Considering only high calcium liming materials, the relative capacities to neutralize soil acidity are: 2000 pounds $CaCO_3 = 1480\ Ca(OH)_2 = 1120\ CaO$. Thus for a practical evaluation, it requires about ½ as much burned lime and ¾ as much hydrated lime to accomplish the same effect as one ton of finely ground limestone. If speed of neutralization is not a factor in deciding which form to purchase, the main consideration is then one of cost per unit of lime oxides delivered to the farm.

OTHER LIMING MATERIALS

Marl is a soft form of calcium carbonate found under peat or muck beds, on the bottom of old lakes, or near stream or shore lines. It arises by the deposition and accumulation of microscopic mollusks or by the precipitation of dissolved calcium carbonate. Frequently it is referred to as "bog-lime" since much of it occurs in swampy areas overlaid by varying amounts of peat and muck. The purity may vary from 50 to 90 per cent calcium carbonate. *Travertine lime* can be included under this classification. It is formed by chemical precipitation of calcium carbonate from lime saturated waters from springs and streams and often contains large quantities of soil material as an impurity. The chief disadvantage of marl and travertine lime is that usually both are sold in the wet state. Transportation costs are greater because of the additional weight of water, and they are difficult to spread uniformly. Some marl producers dry their product partially by air drying for a few weeks, or by heating the marl in rotary kilns, cribs, or heated steel cars. When used in the locality where they are found, if they can be purchased at a reasonable rate in accordance with their purity, both forms can serve as good liming materials.

Oyster shells when finely ground serve as a good liming material since they contain 45 to 50 per cent lime oxides. The industry is limited to certain locations, and much of the material available consists of fine screenings resulting from crushed oyster shells to be used for poultry grit. In addition to the lime oxides, the product contains small amounts of the fertilizer elements nitrogen and phosphorus.

Marble dust is available as liming material in certain areas. Since marble is a metamorphosed limestone, high-grade marble dust is just as satisfactory as limestone if the cost is reasonable.

Other by-product liming materials consumed locally are precipitated lime carbonate from paper mills, acetone plants, sugar factories, gas works, tanneries, and acetylene plants. The main objection to all of these is that they are sold in a wet state, thereby increasing the cost of hauling and difficulty of spreading uniformly. They may be economical only in the immediate localities where they are produced.

Unleached *wood ashes* are used as a means of correcting acidity on a small scale as for home gardens, since they contain 20 to 50 per cent calcium carbonate. In addition, wood ashes may contain over 4 per cent K_2O, particularly if obtained from burning hardwoods.

Blast furnace slag is essentially a mixture of calcium and magnesium silicates and oxides obtained as a by-product of smelting iron ore. Limestone is used as a flux in the production of pig iron, and as the iron ore is reduced to pig iron, the calcium of the limestone combines with the silicates in the iron ore. The silicate containing some oxides is drawn off and then air cooled on a slag dump, or water cooled to produce granulated slag.

Since large quantities of this material are available at little or no cost in the vicinity of steel mills, it can serve as an economical liming material in such localities. On the basis of producing crops, approximately 3 tons of the granulated slag are required to provide the same results as 1 ton of agricultural ground limestone.[57] If the slag were pulverized to equal fineness as the limestone, then 2500 pounds of the pulverized slag would be equivalent to 1 ton of limestone. This grinding process is expensive, however, and material is quite abrasive, so that the granulated slag is usually more economical to use.

METHODS OF DETERMINING SOIL ACIDITY AND LIME REQUIREMENT

Peech and Bradfield [34] recently summarized the more promising chemical methods of estimating lime needs of soils under five categories:

(1) Determination of exchangeable hydrogen.
(2) Rapid determination of lime requirement.
(3) Determination of soil reaction.
(4) Determination of exchangeable calcium and degree of calcium saturation.
(5) Determination of readily soluble iron, aluminum and manganese.

The principles upon which these methods are based, their errors, and their usefulness are adequately discussed by these authors and none of the details will be included here.

Of these methods, the one most frequently used because of its simplicity is the soil reaction test (pH). The lime requirement methods are designed to determine the amount of limestone needed to bring the reaction of the soil to some desired pH as 6.5 or neutrality, either by direct potentiometric titration of the exchangeable hydrogen or by titration of a salt solution extract of the soil. In this latter procedure, the cation of the salt solution replaces the hydrogen ions on the colloidal complex, and the hydrogen ions in the salt solution extract are then estimated by titration.

In order to standardize methods in various soil laboratories, recommended procedures for the determination of soil reaction and exchangeable hydrogen were published recently by the U.S.D.A.[33] Briefly, the recommendations are: (1) pH is to be determined with the glass electrode using a one to one mixture of soil and distilled water after standing one hour, and (2) exchangeable hydrogen is to be determined by replacing the hydrogen ions on the colloidal complex with 0.5 normal barium chloride dissolved in an aqueous 0.2 normal triethanolamine solution adjusted to pH 8.2 as proposed by Mehlich.[26]

In soil testing laboratories, both pH and some rapid lime requirement titration procedure are commonly used. In the field, for farm or garden soils, however, pH is usually determined colorimetrically using indicators and the pH values are translated into lime requirements. Although this latter approach is open to criticism because the buffer capacities of soils vary, where soils have approximately the same texture and organic matter content, a fair approximation of the amount of limestone needed can be estimated. For example, in Pennsylvania, where most of the soils are fine textured, the factor of 350 pounds of limestone per acre for each 0.1 pH unit rise desired usually gives a satisfactory practical recommendation. This is modified where needed, by decreasing the amount $\frac{1}{3}$ to $\frac{1}{2}$ for sandy soils, increasing the amount $\frac{1}{3}$ to $\frac{1}{2}$ for clay soils, and doubling the amount for soils high in organic matter. Of course, the pH requirements of the crop to be sown must be considered in making the recommendation of amount of limestone to be applied.

PRACTICAL CONSIDERATION

Complete discussions of the practical aspects on the use of lime regarding amounts, time and method of application, and forms of lime to apply, are published by most of the Eastern Agricultural Experiment Stations, and the reader is referred to these for his particular locality. Only several general statements will be made here.

The amount of lime to be applied should be determined by a lime requirement determination rather than any rule-of-thumb statement.

Since most plants do best around a pH of 6.5, lime requirements are usually reported on the basis of attaining this pH. The lime needs of the plant to be grown must always be considered since some plants as the Ericaceous group require more acid soils, while other plants as alfalfa and sweet clover prefer a pH of approximately 7. Potatoes are grown in soils with a pH of 5.0 to 5.5 to reduce scab injury. Thus, the common lime requirement recommendations based on attaining a pH of 6.5 must be modified accordingly for any crop that does not do well at pH 6.5.

Requirements are usually stated in terms of pounds of agricultural ground limestone per acre for plow depth. If other liming materials are used, conversions to equivalent amounts of these other materials must be made. The only advantage of burned or hydrated forms of lime is their speed of action and the usual disadvantage of cost. If coarser limestones are used, such as the 4-mesh limestone screenings, the amount of fine material is so small that heavy applications are required (about five times that of agricultural ground limestone) to obtain a satisfactory immediate effect. Of the 8- to 10-mesh agricultural limestone meal, about twice as much would be needed. However, these coarser materials would have a greater lasting effect in the soil.

The most important single factor to consider regarding method of application is that the liming material be distributed uniformly and intimately mixed with the soil. In the vicinity of each particle of liming material, the soil acidity is neutralized, and when the spheres of neutralization overlap within a reasonable time, the maximum desired effect of the lime is achieved. For this reason, burned lime in the lump form is not a satisfactory liming material, and should be ground or slaked properly to effect intimate contact with the soil. If the soil is too wet when either burned or hydrated lime is applied, difficulty in spreading and mixing will be experienced since these forms will ball or later dry into hard crumbs.

If the lime requirement of the soil is high, such as 3 or 4 tons of limestone per acre, it is advisable to split the application and apply half before plowing and half after plowing, or in split applications in two successive years after plowing the soil. With very acid subsoils, it may be advantageous to plow down part of the lime to encourage the penetration of roots into the lower areas. This is particularly true when it is planned to sow a deep rooted legume like alfalfa. When only one application of lime is to be made, it should never be top dressed and plowed down since the neutralized soil will be at the lower half of the plowed layer and not at the surface where it will be needed most. For grasslands, obviously the only practical method of application is by top dressing, and over a period of years the lime will penetrate slowly into the soil. However, for such surface applications, only ½ the lime requirement as usually stated should be applied since the lime is not mixed with the entire plow depth.

It has been shown [2, 27, 42, 56] that frequent small applications give larger returns in crop yields and are thus more economical than equivalent single large applications. Leaching losses of calcium are also considerably less with frequent small applications.[24, 29, 42, 45]

Regarding the time of application, if the soil is appreciably acid, lime gives the greatest initial response when applied preceding the most lime loving crop, such as the legume seeding. Once the lime requirement of the soil is satisfied, it makes very little difference where in the rotation the maintainance applications are made so that lime can be applied at any time when it is most convenient.[58] For potatoes, the recommended practice is to apply any lime needed to maintain a pH not over 5.5, immediately after the potatoes. This involves the use of small amounts of lime, usually not over 500 pounds, the effect of which will not carry over to the next potato crop.

Finally, if any soil deficiency of magnesium is suspected, it is advisable to apply dolomitic limestone rather than high calcium limestone. Surveys of the magnesium content of drainage waters of the United States showed the magnesium content to be low or very low in the Coastal Plain section of Eastern South Carolina and other southern states as well as in the gray sandy areas of the Piedmont Plateau section.[10] Some agronomic investigations [9, 20] have also indicated that soils along the Atlantic coast are becoming deficient in magnesium. In Pennsylvania, corn specialists very recently have begun to suspect that magnesium deficiency may be a more serious problem in some soils than had been previously recognized. Crop yields will be reduced if magnesium is deficient in the soil, even at desirable pH ranges; therefore, magnesium containing liming materials should be recommended in any suspicious areas.

Additional Reading Suggestions

A number of excellent discussions on the importance and use of lime are available in standard soil texts,[3, 6, 10, 23, 30, 50, 51] as well as in specific articles on the subject.[27, 41, 47, 48] In addition, the reader is referred to the recent symposium on calcium published in Soil Science (Volume 65, No. 1), which contains discussions by many authors on the effect of lime upon the soil.

BIBLIOGRAPHY

1. Albrecht, W. A., *Mo. Agr. Expt. Sta. Bull.* **429** (1941).
2. Ames, J. W., and Schollenberger, C. J., *Ohio Agr. Expt. Sta. Mo. Bull.* **2**: 121 (1917).
3. Andrews, W. B., "The Response of Crops and Soils to Fertilizers and Manures." State College, Miss. (1947).

4. Arnon, D. I., and Johnson, C. M., *Plant Physiol.*, **17**: 525 (1942).
5. Association of Official Agricultural Chemists. "Methods of Analyses." Washington, D. C. (1945).
6. Bear, Firman E., "Soils and Fertilizers." New York, John Wiley and Sons, Inc. (1942).
7. Bear, Firman E., and Toth, S. J., *Soil Sci.* **65**: 69 (1948).
8. Bizzell, J. A., and Lyon, T. L., *Proc. and Papers, First Internatl. Cong. Soil Sci.* **2**: 342 (1927).
9. Chucka, J. A., *Am. Potato J.* **11**: 29 (1934).
10. Collings, Gilbeart H., "Commercial Fertilizers." Philadelphia, Pa., Blakiston's Sons and Co., Inc. (1947).
11. De Turk, E. E., *Geol. Survey Circ.* **23**: 191 (1939).
12. Frear, W., *Pa. Dept. Agr. Bull.* **261** (1915).
13. Fried, M., and Peech, M., *J. Am. Soc. Agron.* **38**: 614 (1946).
14. Hartwell, B. L., and Damon, S. C., *R. I. Agr. Expt. Sta. Bull.* **180** (1919).
15. Heim, P. E., *Fert. Rev.* **23** (4): 3 (1948).
16. Hester, Jackson B., *Am. Fert.* **92** (12): 5 (1940).
17. Hilgard, E. W., "Soils." New York, The Macmillan Co. (1906).
18. Hopkins, C. G., "Soil Fertility and Permanent Agriculture." Boston, Ginn and Co. (1910).
19. Kilmer, V. J., Hays, O. E., and Muckenhirn, R. J., *J. Am. Soc. Agron.* **36**: 249 (1944).
20. Knoblauch, H. C., and Odland, T. E., *J. Am. Soc. Agron.* **26**: 609 (1934).
21. Lipman, J. G., Blair, A. W., McLean, H. C., and Prince, A. L., *Soil. Sci.* **15**: 307 (1923).
22. Lyon, T. L., *Cornell Univ. Agr. Expt. Sta. Bull.* **531** (1931).
23. Lyon, T. L., and Buckman, H. O., "The Nature and Properties of Soils." New York, The Macmillan Co. (1948).
24. MacIntire, W. H., *Soil Sci.* **24**: 475 (1927).
25. MacIntire, W. H., Shaw, W. M., Robinson, B., and Young, J. B., *Soil Sci.* **55**: 321 (1943).
26. Mehlich, A., *Proc. Soil Sci. Soc. Am.* **3**: 162 (1938).
27. Midgely, A. R., *Proc. Soil Sci. Soc. Am.* **8**: 329 (1943).
28. Midgely, A. R., and Dunklee, D. E., *Vt. Agr. Expt. Sta. Bull.* **456** (1940).
29. Midgely, A. R., and Weiser, V. L., *Vt. Agr. Expt. Sta. Bull.* **371** (1934).
30. Millar, C. E., and Turk, L. M., "Fundamentals of Soil Science." New York, John Wiley and Sons, Inc. (1943).
31. Naftel, J. A., *J. Am. Soc. Agron.* **29**: 761 (1937).
32. Odland, T. E., and Knoblauch, H. C., *J. Am. Soc. Agron.* **27**: 216 (1935).
33. Peech, M., Alexander, L. T., and Dean, L. A., *U. S. Dept. Agr. Circ.* **757** (1947).
34. Peech, M., and Bradfield, R., *Soil Sci.* **65**: 35 (1948).
35. Pierre, W. H., and Browning, G. M., *J. Am. Soc. Agron.* **27**: 742 (1935).
36. Purvis, E. R., and Davidson, O. W., *Soil Sci.* **65**: 111 (1948).
37. Reed, J. Fielding, and Cummings, R. W., *Soil Sci.* **65**: 103 (1948).
38. Ruffin, Edmund, "An Essay on Calcareous Manures." 2nd ed. Shellbanks, Va. (1835). (Also 5th ed., Richmond, Va. (1852).)
39. Schollenberger, C. J., and Salter, R. M., *J. Am. Soc. Agron.* **35**: 955 (1943).
40. Sherman, G. D., MacHargue, J. S., and Hodgkiss, W. S., *J. Am. Soc. Agron.* **34**: 1076 (1942).
41. Shorey, E. C., *U. S. Dept. Agr. Farmers Bull.* **1845** (1940).
42. Slipher, J. A., *Ohio State Univ. Studies Bull.* **35**: 45 (1927).

43. Smith, G. E., and Hester, J. B., *Soil Sci.* **65**: 117 (1948).
44. Stauffer, R. S., *J. Am. Soc. Agron.* **34**: 830 (1942).
45. Stewart, R., and Wyatt, F. A., *Soil Sci.* **7**: 273 (1919).
46. Truog, E., *Soil Sci.* **5**: 169 (1918).
47. Truog, E., "Soils and Men." U. S. Dept. Agr. Yearbook of Agriculture, pp. 563–580. Washington, D. C., Govt. Printing Office (1938).
48. Truog, E., "Science in Farming." U. S. Dept. Agr. Yearbook of Agriculture, pp. 566–576. Washington, D. C., Govt. Printing Office (1943–7).
49. Truog, E., *Soil Sci.* **65**: 1 (1948).
50. Truog, E., Graul, E. J., and Muckenhirn, R. J., "Soils, Nature, and Management." Mimeographed. Soils Dept., Univ. of Wisconsin (1947).
51. Weir, W. W., "Soil Science." Philadelphia, Pa., J. B. Lippincott Co. (1936).
52. Wheeler, H. J., Hartwell, B. L., and Tucker, G. M., *R. I. Agr. Expt. Sta. Ann. Rept.* **8**: 232 (1884).
53. White, J. W., *Pa. Agr. Expt. Sta. Bull.* **149** (1917).
54. White, J. W., *Commercial Fert.* **66**: 9 (1941).
55. White, J. W., *Pit and Quarry* **39**: 81 (1947).
56. White, J. W., and Holben, F. J., *Pa. Agr. Expt. Sta. Bull.* **211** (1927).
57. White, J. W., Holben, F. J., and Jeffries, C. D., *Pa. Agr. Expt. Sta. Bull.* **341** (1937).
58. Yoder, R. E., *Ohio Agr. Expt. Sta. Agron. Mimeo. No.* **96** (1944).

Chapter XII

MINOR ELEMENT SUPPLEMENTS

E. R. Purvis

Rutgers University, New Brunswick, N. J.

For their normal development, plants are now known to require minute amounts of several nutrients which are not ordinarily contained in the current run of commercial fertilizers and liming materials. Among these elements essential to plants in micro quantities are boron, copper, manganese, molybdenum, and zinc. Until comparatively recent times crops appear to have obtained these minor elements in sufficient amounts from the original supply in the soil, or from the unrefined natural materials utilized as fertilizers. Several factors have operated to exhaust both of these sources of supply.

The advent of improved plant varieties, coupled with new cultural practices, has vastly increased the acre yields of many crops, whereas advances in the science of food preservation and in transportation facilities have greatly intensified the production of vegetables and fruits. This has resulted in an increased demand upon the soil for all plant nutrients which has been met, in so far as the major nutrients are concerned, by the increased use of commercial fertilizers. With the increased use of fertilizer throughout the world, the supply of many of the unrefined natural products, formerly utilized as fertilizer materials, became inadequate, or else found a more profitable market in other uses. Synthetic and refined products replaced the crude and unrefined materials in the manufracture of fertilizers. The nitrogen, phosphorus, and potassium in the synthetic, or refined, materials is just as effective as that in the old, and in most instances sells at a lower unit cost. However, the impurities are largely removed from these new materials and some of these impurities are essential to normal plant growth.

In other instances, the use of liming materials hastened the depletion of the soil's supply of available minor nutrients, either by crop removal in increased yields, or by eliminating the elements from an available condition in the soil solution. Among the first widespread occurrences of a minor nutrient deficiency under field conditions in the United States, to be recognized as such at the time, was that of manganese in Rhode Island in the early 1920's. Spinach growers in this state had become enthusiastic over the response of their crops to applications of lime. As a result many soils were overlimed, and an extreme chlorotic plant condition became prevalent. McLean and Gilbert [71] determined the cause of the disturbance to be a deficiency of manganese and corrected the condition by the application of a weak manganese sulfate spray to the foliage of the plants. Since the disturbance did not appear at soil reactions lower than pH 6.2, it is evident that the lime had affected the availability of the manganese in the soil.

Today it is known that extensive areas of our soils are incapable of supplying plants sufficient amounts of the minor nutrients, and an appreciable tonnage of salts of boron, copper, manganese, and zinc is used annually in soil amendments. There is considerable evidence that molybdenum must be added to the list of essential nutrients deficient in some soils. Cobalt and iodine are required by animals (see chapter XX, Volume I) but have not yet been demonstrated to be essential to plants. Aluminum, selenium, silicon, and sodium are present in the ash of all plants but have yet to be shown to be essential to normal plant growth. There is little reason to doubt that some of the above-mentioned elements, or perhaps others, will eventually be found to be essential to plants, once we have refined our materials and techniques sufficiently to assure that we are not unwittingly supplying the element under study as an impurity to our control culture.

In the remainder of this chapter, the minor elements—boron, copper, manganese, molybdenum, and zinc—will be discussed in separate sections. However, before entering into these discussions it might be well to point out that the term "minor," as applied to the nutrients considered here, refers to the quantity required by plants and in no sense indicates a degree of essentiality less than that of such major nutrients as calcium, nitrogen, etc.

BORON

Because of the extreme abnormal symptoms developed by many plants growing on soils deficient in boron, and the widespread occurrence of such soils throughout the world, boron may be considered the most important of the minor elements from the viewpoint of practical agriculture. It has been known for more than a century that boron is present in the ash of some plants, and as early as 1903 Bertrand[16] recommended that salts of the element be used in agricultural fertilizers. Agulhon[1] concluded in 1910, after exhaustive studies dealing with the growth promoting and stimulating effects of boron upon plants, as well as its toxic properties in relatively low concentrations, that the element was probably essential to the normal growth of certain plants. Maze[66] and later Warrington,[114] employing highly refined techniques not available to their predecessors, finally established the essential role of boron in the nutrition of the maize and broad bean plants respectively. The element was not generally accepted as essential to all plants until the extensive investigations of Sommer and Lipman,[105] and of Brenchley and Warrington,[24] were published in 1926 and 1927. Shive [98] has called attention to the peculiar properties of boron and the great versatility of its compounds as follows:

> "Boron has contributed many items of value to civilization over a period of more than half a century. It is used in the preparation of raw silks for weaving and hides for tanning. It enters into the manufacture of the fine, stain-resisting glaze of the finest potteries and ceramics, and into the making of common and chemically resistant glass. In metallurgy, it plays a prominent part in the production of many alloys. It is used in the preparation of antiseptic solutions, medicated bandages, and cosmetics, and in the manufacture of rayon fabrics. Most glazed papers contain borax in their coatings. It has made nickel plating a practical commercial process and has aided immeasurably in the art and practice of brazing and welding. It is used extensively as a deliming agent in the manufacture of a number of important commercial products. It finds other uses not here enumerated. It has been suggested that the peculiar properties of boron which render it so versatile and make its compounds so useful in the arts and trades are also the ones which render it indispensable in the growth and development of the plant."

The Boron Requirements of Plants. Plants vary over a relatively wide range in their requirements for boron as well as in their tolerance to the element.[13, 83] With no other plant nutrient is there such a narrow range between the amount required for optimum growth and the amount necessary for toxicity. Crops such as alfalfa, beets, cauliflower, celery, and turnips have a relatively high requirement for boron while one-tenth the amount required by these plants will be sufficient for such crops as snap beans, cucumbers, and the small grains. Alfalfa may contain as many as 100 p.p.m. of boron on a dry-weight basis, whereas the normal content of the element in barley and rye plants is less than 5 p.p.m.

The existence of a functional relationship between boron and calcium within the plant has been demonstrated by a number of workers.[23, 58, 65] A low intake of either nutrient causes the plant to require less of the other. Similarly, a high intake of one increases the requirement of the plant for the other. Plants growing on soils of high lime content have a higher boron requirement for each unit of growth because of an increased calcium intake. Similar relationships have been noted between boron and potassium, and between boron and nitrogen.

Symptoms of Boron Deficiency in Plants. Visible symptoms of boron deficiency vary widely between species of plants. In most instances the young growing tissues of the plant are first affected. Roots of plants suffering from insufficient boron fail to develop. Eventually both phloem and xylem tissues disintegrate, resulting in the disruption of the conducting systems of the plant. In extreme cases, plant death may occur, but this rarely happens under field conditions where a complete absence of boron is seldom encountered.

Boron deficiency symptoms affecting many crops were observed and described long before the cause was known. Since no organisms were found as causative agents, and the disturbance could not be transmitted by inoculation to healthy plants, the disease was said to be physiological. Among such physiological diseases of plants, which were later found to be caused by boron deficiency, are "heart rot" of beets,[22] "cracked stem" of celery,[84] "internal cork" of apples,[70] "yellow top" of alfalfa,[31] "brown heart" of turnips,[28] and many others. Today, more than 50 cultivated crops have been reported to suffer from boron deficiency under field conditions and there is every reason to believe that others will be added to this list in the future.

The Boron Content of Soils. According to Clark and Washington,[29] igneous rocks contain 10 p.p.m. of boron. The concentration in sea water has been found to be approximately 4.5 p.p.m.[74] Goldschmidt and Peters[42] found boron to be common as an impurity in many rocks and minerals, and Schaller[93] lists 56 boron containing minerals of which tourmaline, a resistant boroscilicate containing about 3 per cent boron, is probably the most widely distributed in soils.

Cook and Wilson[30] were among the first to determine the boron content of a number of soils. Since their results indicated that topsoils from seven states contained less than 0.25 p.p.m. of boron, it is evident that they extracted but a small part of the boron present. More dependable analyses have been reported by a number of workers.[18, 86, 90, 116] Working with soils from widely separated areas, the results of these investigations indicate that soils contain boron in amounts varying from 2 to more than 100 p.p.m., with the average content falling within the range of 30 to 40 p.p.m.

Perhaps the most extensive work dealing with the boron content of soils is that of Wheatstone, Robinson and Byers,[116] who examined 118 samples of soil, selected as representative of the great soil groups and of the geographical regions of the United States, for total boron content. The element was detected in all samples studied and varied in content from 4 p.p.m. in soils from humid areas to 133 p.p.m. in certain dessert soils. These authors conclude that the boron content of a soil is dependent upon the content of the element in the parent material of that soil and upon the type of weathering this material has undergone. Soils derived from alluvium, limestone, shale, and glacial drift were found to be high in boron, whereas those formed from igneous rock and unconsolidated materials were low in content of the element. Podzols, half bog, muck, and red and yellow podzolic soils were found to be relatively low in boron, while alluvial, gray-brown, podzolic, prairie, chestnut, brown, and chernozem soils were high in content of the nutrient. Acid soluble boron (soluble in 85 per cent phosphoric acid), which the authors assume to represent the maximum available boron, was found to be concentrated in the colloid fraction of the soil and to be constant in the colloid throughout the profile.

Acid soluble boron was found to increase with increasing soil pH. Based on their analyses, these investigators list three major areas of the United States where soils are likely to show boron deficiency as: the Atlantic and Gulf Coasts from Maine to Texas; Northern Minnesota, Wisconsin, and Michigan; and California and the states of the Pacific northwest. In the main these areas correspond with those listed in an earlier publication[83] based on reported occurrence of boron deficiency in crops grown under field conditions.

It is generally accepted that the total boron content of a soil is not a reliable measure of the ability of that soil to supply boron to plants. Various solvents have been suggested to extract that fraction available to plants of which the hot water method of Berger and Truog[14] is perhaps most generally employed today. The amount of boron extracted by this procedure has been found to correlate well with field observations of plant symptoms of deficiency and response. Some investigators[86] consider 0.35 p.p.m. of hot water-soluble boron in the soil as the critical point below which plants suffer for lack of the nutrient.

Soil Factors Affecting the Availability of Boron to Plants. The lime status of the soil is generally considered to be the most important factor affecting the availability of boron to plants.[76] When sufficient lime is applied to an acid soil to increase the reaction above pH 6.0, a deficiency of available boron will often result. This may be brought about in two ways; the application of lime may so stimulate microbial and plant growth that the limited supply of boron originally present is soon depleted, or liming may remove the boron from the soil solution through fixation in an insoluble compound, or compounds.

The application of boron containing salts to soils has been found to stimulate the growth of soil microbes.[44, 76] Since liming also increases the rate of growth of these organisms, they compete with plants for the available boron supply. Moderate applications of lime to many of the light-textured acid soils of the Atlantic Coastal Plain have produced severe boron deficiency symptoms in crops, although it has been demonstrated that the lime did not affect the water-soluble boron content.[43, 86] Such soils simply do not contain sufficient available boron for optimum plant growth.

Excessive liming of acid soils, with a resulting increase in soil reaction to neutrality or above, will often produce boron deficiency through fixation of the available boron. There is evidence that this fixation is a function of the soil organic matter which assumes a high fixing capacity for boron once it is activated by lime.[73] Also, the higher the organic matter content of a soil, the greater the amount of applied boron containing salts required to produce toxicity in plants. Often this fixation of boron is so rapid and complete that it is impossible to supply plants growing on these soils with sufficient amounts of the nutrient through ordinary soil amendments with salts of the element. This is essentially true in instances where the soil reaction approaches pH 8.0. Under these conditions boron must be supplied to plants by spraying weak solutions of either borax or boric acid upon the foliage.

Supplementing the Soil's Supply of Boron. Because of the fertilizer industry's experience with the toxic effects of boron contained in unrefined potash salts during World War I, interest in boron was centered, until about ten years ago, in studies of the toxic properties of the element and in methods of refinement for removing the unwanted boron from fertilizer materials. It is probable that the unfortunate experiences of this period delayed the establishment of boron as an essential plant nutrient by at least a decade. Once boron deficiency was established as the cause of the physiological disturbances in plants, mentioned in the previous section, the practice of supplying the nutrient to deficient soils through small applications of borax, or boric acid, spread rapidly.

There appears to be very little accumulation of applied boron in soils, and annual applications of the nutrient may have to be made to deficient soils. Because of the variation in boron requirements of various plants, it is impossible to add a constant quantity of the element to all fertilizers to satisfy the needs of all crops. Likewise, the texture of the soil, the organic matter content and the soil reaction will influence the amount that must be applied to a given soil. Where 10 pounds of borax per acre is sufficient for celery on the light sandy soils of Florida, 100 pounds to the acre is required for the same crop on Michigan peat soils. Ranges in recommendations for representative crops are illustrated in Table 92 below:

TABLE 92. AMOUNT OF BORAX RECOMMENDED FOR CROPS GROWN ON BORON DEFICIENT SOILS [83]

Crop	Pounds Borax per Acre	Crop	Pounds Borax per Acre
Alfalfa	10 - 50	Lettuce	10
Apples	0.25 to 1 lb. per tree	**Mangels**	10
Beets	10 - 50	**Pears**	0.5 lb. per tree
Broccoli	10	**Potatoes**	10 - 25
Cabbage	10	**Radishes**	10 - 20
Carrots	10 - 20	**Rutabagas**	10 - 25
Cauliflower	10 - 25	**Strawberries**	10
Celery	10 - 100	**Sugar beets**	10 - 40
Corn	10	**Sweet potatoes**	5 - 10
Cotton	0.5 - 10	**Tobacco**	0.5 - 10
Eggplant	10 - 20	**Tomatoes**	10 - 20
Grapes	10	**Turnips**	10 - 30

COPPER

In early observations of the stimulating effects of copper applications upon plant growth, apparently the possibility of the element being an essential nutrient was not considered. In 1912 Lutman,[64] and Stewart, French, and Sirrine[107] reported increased yields of potatoes from the use of Bordeaux mixture as a spray material. Since potato blight, the disease for which the fungicide was used, failed to develop in the unsprayed plots, they attributed the increase in yield to the stimulating effects of copper. In 1917, Floyd[38] recommended copper sulfate applications to the soil, or the use of Bordeaux sprays, for the control of "dieback" of citrus, a disease described by Swingle and Webber[108] in 1896 and considered by them to be due to malnutrition. In this plant disorder the terminal branches are primarily affected and tend to die back from the tip. Today the disturbance is known to occur wherever citrus is grown and has been reported as affecting avocados,[92] olives,[101] and various deciduous trees such as apple, apricot, peach, pear, plum, and tung.[80, 84]

According to Jacks and Scherbatoff,[54] Ritzema in 1925 was the first to demonstrate that applications of copper sulfate would control "reclamation disease," a condition prevalent on recently reclaimed heath and moorland soils of Europe. Plants growing on these soils were subject to marked chlorosis and a diminution of turgor. Tips of leaves of cereals turned pale green or white, and affected plants frequently failed to produce seed. The most susceptible crops were cereals, beets, and various Papilionaceae. The disease was believed to be due to the accumulation of a toxic organic substance produced by the waterlogged conditions often existing in these soils. Smith, cited by Sommer,[104] succeeded in isolating such a substance from the hot alcohol extract of a black moor soil. He named the substance "gliedine" and demonstrated that typical symptoms of "reclamation disease" were produced in plants growing on soils to which "gliedine" had been added. Although other investigators soon demonstrated that the application of copper salts to organic soils resulted in an increased copper content in plants growing on these soils, the possibility that "gliedine" may produce copper deficiency through the fixation of copper in the soil, or within the plant, has been suggested. This possibility has neither been established nor refuted.

In 1927, Allison, Bryan and Hunter[4] obtained striking response in the growth of a large number of plants when copper sulfate was applied to the raw peat soils of the Florida Everglades, and Felix[35] reported that applications of copper sulfate made possible the growth of onions and lettuce on unproductive peat soils in New York.

It is of interest to note that the above instances of the use of copper sulfate to correct unproductive soil conditions predated the establishment of copper as an essential plant nutrient. It was not until 1930–1931 that Sommer [102, 103] published data which conclusively demonstrated that copper was an essential nutrient for the normal growth of plants.

Today copper deficiency is known to occur in a wide variety of plants and a considerable tonnage of copper sulfate is applied annually to deficient soils throughout the world.

The Copper Requirements of Plants. From the data on the mineral composition of plants compiled by Beeson,[13] it is evident that the copper content of plants seldom exceeds 25 p.p.m. The highest copper content reported in these tables is that for Florida grown celery (560 p.p.m.), and since this crop is sprayed weekly with Bordeaux mixture it is likely that this content is not normal for the celery plant. Plants growing on Australian soils rich in copper have been reported to contain in excess of 500 p.p.m. copper.[47]

The functions of copper within the plant remain obscure. According to Sommer,[104] the most fertile field of investigation concerning the function of the element has been in the realm of enzymes. Catalytically active copper-protein complexes have been isolated from a number of plant sources and have been found to possess a considerable degree of specificity.[32, 60, 79]

Neish [76a] found copper to be concentrated in the chloroplasts of leaves, reporting that 74.6 per cent of the total copper content of leaves of *Brifolium pratens* was contained in the chloroplasts. Bergman and Truran,[15] and Orth et al.,[77] found marked increases in the chlorophyll content of plants treated with copper salts when compared to that of untreated plants, the latter investigators reporting a better than fourfold increase in the case of citrus leaves. The role of copper in chlorophyll formation is believed to be an indirect one,[104] or else some other function is sooner, or more seriously, affected by a deficiency of the element, for some deficient tissues have been found to contain more copper than normal tissues.[10]

Symptoms of Copper Deficiency in Plants. Symptoms of copper deficiency are quite variable in different plants. Although some form of leaf chlorosis usually occurs in plants affected by the deficiency, there are some plants where no change in color can be detected and others where the leaves develop a darker shade of green. The dying back of the young growing tips in deciduous fruits appears to be a common deficiency symptom with this group of plants. This is usually accompanied by rosetting, or bushy growth, of leaves just below the dead areas of the twigs. Chlorosis, when present, is sometimes confined to the older leaves. The formation of gum pockets has been noted in citrus. Several publications contain excellent photographs of copper deficiency symptoms in a number of representative plants.[39, 82, 122]

The Copper Content of Soils and Factors Affecting Its Availability to Plants. Soils vary in content of copper from less than 1 to about 50 p.p.m., yet plants are able to obtain the small amount of the nutrient required for normal growth from most soils.

The available copper content of soils is primarily dependent upon two factors. In acid soils the soluble copper may be lost through leaching, whereas in alkaline soils the element is apparently fixed in an unavailable state. Bryan[25] states that copper deficiency in Florida citrus is more prevalent on acid than on alkaline soils, and Harmer[46] obtained greater response from applied copper on the muck soils of Michigan when the pH was below 6.0, although a few crops gave response when the pH was above 7.0. Australian workers[87, 109] have reported response to applied copper on very acid mucks as well as on calcareous soils. Williams[118] obtained plant injury from an application of 50 pounds of copper sulfate per acre to an unlimed North Carolina soil, and no effect from copper applied at the same rate when the soil was limed with 2 tons of limestone to the acre. However, when an application of 6 tons of limestone per acre was made, a decided response to applied copper was noted.

Correcting Copper Deficiency in Soils and Plants. Copper deficiency in plants may be corrected by soil treatment with copper sulfate or through the use of sprays containing copper (Bordeaux mixture, etc.).[64, 107] The latter method produces quicker recovery and is widely employed with tree crops. Where copper sulfate is applied to the soil, 30 pounds of the material to the acre has been found to be sufficient for most soils. Peat soils[46] may require larger amounts while as little as 10 pounds to the acre has been found to be injurious to some crops growing on very sandy, or gravelly, soils of low buffer capacity.[117]

MANGANESE

Even before manganese was isolated in the pure form, Scheele[94] found the new element to be a common constituent of rocks, soils, and plants. He detected manganese in the ash of all plants examined but apparently drew no conclusions as to whether or not the element was essential to plant growth. Because of the difficulty of separating the salts of iron and manganese, the establishment of the essential role of the latter element in plant nutrition was delayed until the work of McHargue and his associates, begun in 1912 and reported in a long series of papers.[68] Their findings have been substantiated by other investigators and today manganese is accepted as an essential nutrient for higher plants.

Sjollema and Hudig[99] were probably the first to demonstrate that the unproductiveness of certain Dutch soils could be corrected by the application of salts of manganese. They found that the physiological disorder in oats, known as "grey speck," disappeared after soil treatment with manganese salts. During the past two decades manganese-deficient soils have been found throughout the world. As mentioned previously, the first report of such soils in the United States came from Rhode Island where is was found that "yellows" of spinach was corrected by the application of manganese salts.[71] Four years later, Allison[3] reported response in several crops to applications of manganese on the peat soils of the Florida Everglades. Since these soils are underlain with marl and have been subjected to frequent surface fires in the past, their reaction varies from slightly acid to alkaline. From the number of reports from all parts of the world citing the beneficial effects obtained from the application of manganese salts to alkaline organic soils, it appears to be a safe conclusion that the unproductiveness of all such soils is due, at least in part, to a deficiency of manganese.

Although manganese deficiency is especially common in organic soils, mineral soils deficient in the nutrient have been reported from practically every truck crop growing area along the Atlantic seaboard and from other sections of the country. Usually the deficiency in mineral soils is associated with an excessive use of lime on normally acid soils. Natural limestone and marl soils may or may not be deficient in the nutrient, depending upon factors which are little understood at present.

The Manganese Requirements of Plants. The manganese content of plants is always low as shown by the data in Beeson's[13] tables where the percentage of the element in plants seldom exceeds a few hundredths of 1 per cent on the dry weight basis. However, these data show a wide variation in manganese content between various plants, and within the same species of plant grown on different soils. The range in this variation is greater than that for most of the other plant nutrients. According to McHargue,[68] leguminous plants usually contain the smallest amounts of manganese, while the grasses contain the highest. Bailey and Anderson[9] report the manganese content of tobacco grown in Connecticut to vary from 70 to 2262 p.p.m., the latter amount being toxic to the plants. Soils sufficiently high in soluble manganese to produce crop injury have also been reported from Hawaii[57] and Kentucky.[21]

Various functions within the plant have been attributed to manganese. McHargue[67] concludes from his extensive studies with the nutrient that manganese, along with iron, functions in the synthesis of chlorophyll. Sommers and Shive[106] have demonstrated that manganese influences the oxidation-reduction system within the plant and that this in turn controls the mobility of iron within the plant tissues. Sherman[95] found deposition of ferric iron to occur in the veins of pea leaves from a manganese deficient plant but could detect no ferric iron in similar tissues from normal plants. In this connection it is interesting to note that

Johnson[57] found that sprays containing soluble salts of iron were effective in counteracting manganese toxicity in pineapples. This indicates that the injury attributed to manganese toxicity may actually be the result of a deficiency of active iron.[106] Conversely, manganese deficiency symptoms may be the result of iron toxicity although this suggestion is not so well supported by data.

Rudra,[91] Hester,[48] and Sherman[95] have concluded from their studies that manganese influences the synthesis of ascorbic acid.

Manganese Deficiency Symptoms in Plants. Manganese deficiency symptoms have been described for a wide variety of plants, and an excellent publication showing many of these symptoms in color, along with symptoms of other nutrient deficiencies, is available.[122]

With most plants, the first symptom of manganese deficiency is the development of a chlorotic condition in the leaf areas between veins while the veins themselves remain green. As the deficiency becomes more pronounced the color of the chlorotic areas changes from light green to yellow, or to greyish-white. Brown necrotic spots eventually appear in the affected tissues, or these necrotic areas may become transparent as in spinach where, with recovery, the affected tissue may drop out, leaving clean cut holes as if the leaf had been attacked by chewing insects. Even in the final stages of the deficiency some green color will remain in the network of main veins. Net-veined and paralleled-veined leaves are affected alike by the deficiency.

The Manganese Content of Soils and Factors Affecting Its Availability to Plants. The manganese content of normal soils falls within the range of 0.01 to 0.30 per cent. This closely approximates the soil's content of phosphorus, a nutrient required by plants in much greater quantity than is manganese. Few plants require more than 100 p.p.m. of manganese[13] (on dry weight basis), yet crops are often unable to obtain even this small amount from soils containing several hundred pounds of the element in the surface layer of an acre. Obviously the total manganese content of the soil cannot be used as a criterion of the availability of the nutrient to plants.

Of the several factors which influence the availability of manganese in the soil, that of soil reaction is perhaps the most important. Deficiency of this nutrient is seldom due to a deficiency in total manganese content and seldom occurs on soils more acid than pH 6.5, although deficiencies have been observed on the light sandy soils of the coastal area of the Carolinas at reactions below pH 6.0.

The mechanism by which the soil reaction influences the availability of manganese is not thoroughly understood. It is generally agreed that manganese exists in the soil in an oxidation-reduction system and that only the reduced form of the element is available to plants.[62, 95] It is also agreed that the liming of acid soils favors the oxidation processes in this equilibrium and results in a decrease in the manganous manganese content of the soil. Some attribute this to the strictly chemical oxidation of the manganous ions to hydrated manganic oxide, or to inert maganic oxides. Others consider the oxidation to be essentially a function of soil microbes and have reported data to show that the oxidation of the manganous ions is not affected by the addition of lime to sterile soil.

Leeper[62] concludes that the water-soluble and replaceable manganese contents of soils are not true criteria of the ability of a soil to supply the nutrient to plants. Part of the oxidized manganese was found to exist in an easily reducible state. Soils containing very little water-soluble or replaceable manganese will often contain several hundred parts per million of manganese which may be reduced readily and extracted with neutral ammonium acetate containing 0.2 per cent hydroquinone. This is the manganese fraction which interferes with pH determinations by the hydroquinone method in certain soils. Soils containing appreciable amounts of easily reducible manganese seldom become deficient in available manganese since plants appear to be able to utilize the nutrient from this easily reducible fraction. A laboratory method for detecing manganese deficient soils has been suggested,[61, 96] based on determinations of the water-soluble, replaceable, and easily reducible fractions coupled with an an estimation of the fixing capacity of the soil for manganese. Some soils have such high oxidizing capacities for the element that large applications of manganese will be oxidized to the manganic state within a few hours.[95]

Under field conditions, manganese deficiency in many crops will often correct itself without treatment, or it will occur sproadically on some overlimed soils, appearing one season and being absent the next. It is likely that the explanation of the phenonemon lies in one of two factors, or possibly in a combination of the two.

It has long been known that the pH of the soil is seldom constant throughout the root zone of plants. Not only does the reaction of a soil vary with depth but it may also vary within a single small granule. This variation will often exceed a full pH unit within the distance of a fraction of a centimeter. The value arrived at in normal pH determinations is an average for a composite sample and is actually a median of the values of a number of small pockets of soil of varying degrees of acidity or alkalinity. As long as a sufficient number of acid pockets (below pH 6.5) exist in a soil, plants can obtain their manganese, and other nutrients made unavailable by liming, from these acid areas. When these acid pockets are eliminated, as happens when heavy rains temporarily saturate the soil, or when drought reduces the moisture content of the acid areas to the extent that roots are no longer able to obtain nutrients from this source, manganese deficiency will occur. The deficiency will disappear with the re-establishment of the acid areas by the return of normal moisture conditions. The impossibility of thoroughly incorporating lime into soils, the oxidation of sulfur-containing minerals of sulfur from spray residues, the exudation from roots and the production of acids in the decomposition of organic materials are some of the factors which account for the small areas of varying acidity in soils.

The production of anaerobic conditions in the soil is the second factor which may account for the spontaneous recovery of plants growing on manganese deficient soils. Such conditions may be produced by heavy rains, by continuous light rains, or by flooding. With the oxygen supply of the soil thus limited, part of the soil manganese is reduced to the available manganous state.

Correcting Manganese Deficiency in the Field. Manganese deficiency in field crops can be corrected in three ways. The application of manganese sulfate directly to the soil is perhaps more generally employed. The amounts recommended by various investigators vary from 50 to 100 pounds per acre for mineral soils [2, 71] up to 400 pounds per acre for strongly alkaline peats.[illegible] Mixing the manganese sulfate with two or three times its weight of sulfate of ammonia, or an equal weight of sulfur, has been found to speed up the recovery of crops affected with the deficiency.

Where feasible, the most economical method of supplying manganese to deficient plants is through spraying a weak manganese sulfate solution directly to the foliage of the plants.[71, 111] This method is widely employed with citrus in both California [78] and Florida.[27]

The third method has only limited application. It is the flooding of soils, thereby producing anaerobic conditions under which a fraction of the oxidized manganese is reduced to the available form. This method is practical only where irrigation is possible.

MOLYBDENUM

Molybdenum is the latest addition to the list of chemical elements known to be essential to the normal growth of plants. Probably due to the fact that only limited areas of soils have been found to respond to applications of molybdenum salts, investigators dealing with this plant nutrient are limited to a relatively few locations.

Ter Meulin [110] was among the first to investigate the molybdenum content of soils and plants. He found the element present in all plant tissues examined, the quantity varying from 0.01 to 9.0 p.p.m. The higher amounts were found in seeds of leguminous plants. Fertile soils contained from 0.1 to 0.3 p.p.m. of molybdenum, whereas moor soils contained but one-tenth this amount. Barren sands were found to contain as low as 0.005 p.p.m. of the element.

Working with several crops grown on Canadian soils, Dingwell et al.[33] were unable to detect molybdenum in many of the plant specimens examined. However, they found the element present in several species of plants growing on a soil in which they could not detect molybdenum. These investigators [33] pointed out some of the complications involved in the spectroscopic determination of the minute quantities of molybdenum present in soils and plants.

Arnon [6, 7] observed that the addition of very small amounts of molybdenum to culture solutions improved the growth of barley plants, and that the growth of asparagus and lettuce was stimulated by a mixture of seven metal elements which included molybdenum. Following up this work, Arnon and Stout [8] prepared a highly purified nutrient solution containing the eleven mineral elements known to be essential to plant growth, but no molybdenum. After a few weeks' growth in this solution, tomato plants developed symptoms that were different from those of other nutrient deficiencies so far described. The lower leaves developed a peculiar mottled chlorosis. In advanced stages of the deficiency the margins of affected leaves curled upward, marginal necrosis appeared, and most of the blossoms dropped without setting fruit. The addition of molybdenum to the cultures at a rate of 0.01 p.p.m. was sufficient to correct the condition.

In other solution culture investigations,[17, 20, 51, 115] the beneficial effects of low concentrations of molybdenum have been noted in lettuce, oats, peas, and plums. Similar effects have been reported with some of the lower forms of plant life. The element has been found to be essential to the normal growth and sporulation of *Aspergillus niger* and has been reported to influence greatly the fixation of nitrogen by *Azotobacter*.

Molybdenum Deficiency in Field Soils. Bortels [19] was probably the first to observe response to molybdenum applied to field plots. He reported both qualitative and quantitative response in several leguminous crops and noted a significant increase in the production of alfalfa seed where molybdenum was supplied the plants.

Piper [91] and Trumble [113] have reported response of alfalfa and subterranean clover to molybdenum applications, and Trumble indicates that soils deficient in molybdenum may be fairly common in certain areas of Australia. It seems likely that at least part of the effect of molybdenum deficiency in legumes is due to the role of the element in symbiotic nitrogen fixation. Symptoms of molybdenum deficiency in legumes have been observed to disappear when nitrogen was applied to the plants.

Instances of molybdenum deficiency in field soils have been reported recently from California, New Jersey, and New York. Alfalfa, cauliflower, potatoes, and tomatoes are the crops that have been affected in one or more of these states. An application of ammonium or sodium molybdate, at the rate of 0.5 pound to the acre, has been found to be sufficient to correct the deficiency. It is likely that molybdenum-deficient soils are far more common than is known at present.

There have been reports of cows and sheep being poisoned from eating herbage grown on soils of high molybdenum content. Warrington[114] has described the symptoms of molybdenum toxicity in the potato and tomato. She found barley much more tolerant to molybdenum than potatoes and tomatoes.

ZINC

Raulin[85] was among the first to observe the beneficial effects of zinc upon the growth of plants. Working with *Aspergillus niger* he reported in 1870 that the growth of the fungus was greatly stimulated by the addition of zinc salts to the nutrient solution. Javillier[56] and Maze[66] enlarged upon Raulin's findings and extended the investigations to higher plants during the early years of the present century. Javillier was probably the first to recommend the use of zinc salts as fertilizer materials for field crops. The importance of these early observations were minimized until the work of Sommer and Lipman,[105] reported in 1926, finally established zinc as an essential nutrient for normal growth of several of the higher plants. A year later, Allison, Bryan and Hunter[4] observed plant response to applications of zinc salts in field trials with corn, peas, soybeans, sugar cane, and several other crops grown on the peat soils of the Florida Everglades. In 1929 Roberts and Pierce[88] reported that the use of a zinc-lime spray as a fungicide for peaches resulted in the production of greener and more vigorous leaves.

Investigators were not long in extending these studies to field problems. Physiological disturbances in a number of crops were soon determined to be due to a deficiency of available zinc in the soil. In 1932 and 1933 several thousand acres of tung trees in Florida were treated with salts of zinc to correct a condition which produced a bronzing of the leaves.[26] "Little leaf," or "mottle leaf" of citrus, "rosette" of peaches and pecans, and "white bud" of corn are other plant disorders which were corrected by applications of zinc salts, while significant increases in yield were obtained with many other crops not showing distinct deficiency symptoms.

The Zinc Requirements of Plants. From the limited data available on the subject plants appear to vary markedly in their normal requirements for zinc. Normal leaves of citrus have been found to contain from 25 to 50 p.p.m.[40] of the element while deficient leaves often contain less than 10 p.p.m. Rogers, Gall and Barnette[89] found weeds growing on old cotton soils to contain as much as 700 p.p.m. of zinc, whereas crotolaria growing on the same soil contained but 4 to 11 p.p.m. McHargue and

Roy [69] reported zinc present in the leaves of 23 species of deciduous trees. Because of the difficulties involved in the quantitative determination of the small amounts of the element present in plants, many analyses have been reported on the purely qualitative basis. No instance is known of a failure to find zinc present in the ash of plants where sufficiently refined methods of analysis have been employed. It is likely that the average content of the nutrient in all plants is less than 50 p.p.m. on the basis of dry weight.

The function of zinc within the plant remains pretty much a matter of speculation. Data have been published which show that zinc influences the auxin content of plants,[100] and the peroxidase and catalase activities of plant tissues.[52] Bean [12] found the synthesis of protein and starch to be retarded in zinc deficient plants. Zinc deficiency usually produces some form of leaf chlorosis, and the application of zinc salts results in the recovery of the normal green color in the leaves. This indicates that the element plays a part in chlorophyll formation, or in the preservation of chlorophyll within the leaf.[26]

Symptoms of Zinc Deficiency in Plants. Certain characteristic symptoms of zinc deficiency appear to be common to most plants suffering from an insufficient supply of the nutrient, while specific plants may develop additional symptoms peculiar to the particular species.[122] Among the symptoms common to most plants may be listed the light-green to white mottling of the intravenal areas of the leaves, the appearance of necrosis in these mottled areas, the production of small narrow leaves on spindly twigs; the rosetting of terminal leaves, malformation of leaves, and early defoliation. Additional symptoms which have been reported for specific plants include the production of reddish-purple and bronze pigmentation in peach and tung trees,[75] and of a light yellow to white color in the bud leaves of corn.[11]

The Zinc Content of Soils and Factors Affecting Its Availability to Plants. Zinc is probably present in all soils but the content is always low, varying from 2 to 50 p.p.m. Light sandy soils of low organic matter content contain less of the element than do heavier clays and loams. In a study of the distribution of zinc in different sized soil particles Hibbard [49] found the smaller particles to be considerably richer in the element than the larger particles. Jones, Gall, and Barnette [59] state that zinc exists in soils in three conditions—water-soluble, exchangeable, and a relatively insoluble fraction composed of phosphates, carbonates and silicates, or other stable compounds.

Among the factors which have been suggested as influencing the availability of zinc to plants, that of the soil reaction is perhaps best supported by data. In 1917, Floyd [38] described a physiological disturbance in citrus which resulted from the excessive use of lime on certain Florida soils. The described symptoms are now recognized as those of "frenching," a disorder which is readily corrected by spraying weak solutions of zinc salts upon the foliage of affected trees. This early observation of the influence of soil reaction upon the occurrence of zinc deficiency, although it was not recognized as such at the time, has been amply corroborated by subsequent work. Camp[26] states that zinc deficiency can be expected in citrus when the soil reaction exceeds pH 6.0, either naturally or from overliming, and that there is at least circumstantial evidence to support the theory that at soil reactions in excess of pH 7.85 the element may again become available to plants. Lott[63] has demonstrated that zinc toxicity is reduced when the soil is limed above pH 6.5, and Fudge[26] found a marked reduction in zinc intake by plants from sandy soils as the pH increased from 4.5 to above 7.0.

The nature and quantity of organic materials in the soil greatly influence the availability of zinc to plants. Barnette et al.,[11] working with Florida soils, demonstrated that the beneficial results obtained from the application of manure to tung trees was due primarily to the zinc contained in the manure. Corn grown in rotation with native weeds on these soils exceeded in yield that grown in rotation with crotolaria, a highly recommended green manure crop. Upon analysis it was found that the weeds contained an average of 140 p.p.m. of zinc while the crotolaria contained but 8 p.p.m.

Zinc deficiency on acid soils can normally be attributed to the cropping out of the available zinc supply of the soil and the failure to replenish this supply through fertilization with zinc containing materials. However, Peech[80] and Jamison[55] have reported evidence that on some acid sandy soils of low organic matter content applied zinc may combine with some of the organic constituents to form fairly insoluble compounds.

Because of the low zinc content of soils it is evident that any factor which retards the root development of plants, and thereby restricts the feeding zone, will be conducive to the occurrence of zinc deficiency. Among such factors may be listed waterlogging, the cutting of roots in plowing, drought, and excessive pruning.

Supplementing the Soil's Supply of Zinc. In the past we have unwittingly replenished the soil's supply of zinc through the use of animal manures and the natural organic materials in fertilizers. It is probable that in many instances at least part of the benefits derived from the use of these materials was due to their zinc content. Current methods for supplying zinc to crops growing on soils deficient in the nutrient include the direct application of zinc salts to the soil, and the spraying of weak solutions of these salts upon the foliage of the plants. Soil applications[11] (usually 20 to 30 pounds of zinc sulfate per acre) are normally effective on acid soils, while better results from spraying are obtained on soils having a pH in excess of 6.5. Since zinc deficiency is more common on slightly acid, or alkaline soils, the spray method is more generally used. A common formula in Florida [112] calls for from 2 to 5 pounds of zinc sulfate (89 per cent) to 50 gallons of water. Zinc is compatible with Bordeaux mixture, and, where this material is applied in a normal spraying program, an operation can be saved by including the zinc with the Bordeaux.

BIBLIOGRAPHY

Specific References

1. Agulhon, H., *Compt. rend.* **150**: 288 (1910).
2. Albert, W. B., *S. Carolina Agr. Expt. Sta. Ann. Rept.* **44**: 46 (1931).
3. Allison, R. V., *Fla. Agr. Expt. Sta. Ann. Rept.* (1929).
4. Allison, R. V., Bryan, O. C., and Hunter, J. H., *Fla. Agr. Expt. Sta. Bull.* 190 (1927).
5. Anderssen, F. G., *J. Pomol. Hort. Sci.* **10**: 130 (1932).
6. Arnon, D. I., *Soil Sci.* **44**: 91 (1937).
7. Arnon, D. I., *Am. J. Bot.* **25**: 322 (1938).
8. Arnon, D. I., and Stout, P. R., *Plant Physiol.* **14**: 599 (1939).
9. Bailey, E. M., and Anderson, P. J., *Conn. Agr. Expt. Sta., Tobacco Sta. Bull.* 10 (1928).
10. Bailey, L. F., and McHargue, J. S., *Am. J. Bot.* **30**: 559 (1943).
11. Barnette, R. M., Camp, J. R., Warner, J. D., and Gall, O. E., *Fla. Agr. Expt. Sta. Bull.* 292 (1936).
12. Bean, R. S., Ph.D. Thesis, Univ. of Calif. (1942).
13. Beeson, K. C., *U. S. Dept. Agr. Misc. Publ.* 369 (1941).
14. Berger, K. C., and Truog, E., *Soil Sci.* **57**: 25 (1944).
15. Bergman, H. F., and Trueran, W. E., *Mass. Agr. Expt. Sta. Bull.* 339 (1937).
16. Bertrand, G., *Chem. Zeit.* **49**: 613 (1903).
17. Bertrand, D., *Compt. rend.* **211**: 512 (1940).
18. Bertrand, G., and Silberstein, L., *Compt. rend. Acad. Agr.* **25**: 593 (1939).
19. Bortels, H., *Arch. Mikrobiol.* **1**: 333 (1930).
20. Bortels, H., *Arch. Mikrobiol.* **8**: 13 (1937).
21. Bortner, C. E., *Soil Sci.* **39**: 15 (1935).
22. Brandenburg, E., *Phytopath. Zeit.* **31**: 499 (1931).
23. Brenchley, W. E., and Warrington, K., *Ann. Bot.* **41**: 167 (1927).
24. Brenchley, W. E., and Warrington, K., *Nature* **149**: 196 (1942).
25. Bryan, D. C., *Fla. Dept. Agr.* (*new ser.*) 93 (1940).
26. Camp, A. F., *Soil Sci.* **60**: 157 (1945).
27. Camp, A. F., and Peech, M., *Proc. Am. Soc. Hort. Sci.* **36**: 81 (1938).
28. Chittenden, E., and Copp, L. G. L., *New Zealand J. Sci. Tech.* **19**: 372 (1937).
29. Clark, F. W., and Washington, H. S., *U. S. Geol. Sur., Prof. Paper* 127 (1924).
30. Cook, F. C., and Wilson, J. B., *J. Agr. Research* **13**: 451 (1918).
31. Cook, R. L., *Soil Sci. Soc. Am. Proc.* **2**: 375 (1937).
32. Dalton, H. R., and Nelson, J. M., *J. Am. Chem. Soc.* **60**: 3085 (1938).
33. Dingwell, A., McKibbin, R. R., and Beans, H. T., *Can. J. Research* **11**: 32 (1934).
34. Drosdorf, M., and Dickey, R. D., *Proc. Am. Soc. Hort. Sci.* **42**: 79 (1943).
35. Felix, E. L., *Phytopath.* **17**: 49 (1927).
36. Ferguson, W. S., Lewis, A. H., and Watson, S. J., *Nature* **141**: 553 (1938).

37. Floyd, B. F., *Fla. Agr. Expt. Sta. Bull.* **137**: 161 (1917).
38. Floyd, B. F., *Fla. Agr. Expt. Sta. Bull.* **140** (1917).
39. Forsee, W. T., Jr., *Proc. Soil Sci. Soc. Fla.* **2**: 53 (1940).
40. Gaddum, L. W., Camp, A. F., and Reuther, W., *Fla. Agr. Expt. Sta. Ann. Rept.* **1936**, p. 82.
41. Garner, W. W., *U. S. Dept. Agr., Bur. Plant Ind. Ann. Rept.* **1935**, p. 25.
42. Goldschmidt, V. M., and Peters, C. L., *Gessell. Wiss. Göttingen. Math.-phys. Kl. Nachr.* **5**: 402 (1932).
43. Hanna, W. J., and Purvis, E. R., *Am. Fert.* **91**, No. 8: 1 (1939).
44. Hanna, W. J., and Purvis, E. R., *Soil Sci.* **52**: 275 (1941).
45. Harmer, P. M., *Mich. Agr. Expt. Sta. Sp. Bull.* **314** (1941).
46. Harmer, P. M., *Better Crops With Plant Food* (April 1941).
47. Heckel, E., *Bull. Cos. Bot.* (France) **46**: 42 (1899).
48. Hester, J. B., *Soil Sci. Soc. Am. Proc.* **6**: 243 (1941).
49. Hibbard, P. L., *Hilgardia* **13**, No. 1 (1940).
50. Hill, H., *Sci. Agr.* **17**, No. 3: 148 (1936).
51. Hoagland, D. R., *Proc. Am. Soc. Hort. Sci.* **38**: 8 (1940).
52. Hoagland, D. R., *Soil Sci.* **60**: 119 (1945).
54. Jacks, G. V., and Scherbatoff, H., *Imp. Bur. Soil Sci.* (England) *Tech. Com.* **31** (1934).
55. Jamison, V. C., *Soil Sci. Soc. Am. Proc.* **8**: 323 (1943).
56. Javillier, M., *Internatl. Cong. Appl. Chem. Orig. Commun.* **15**: 145 (1912).
57. Johnson, M. D., *Hawaii Sta. Bull.* **52** (1924).
58. Jones, H. E., and Scarseth, G. D., *Soil Sci.* **57**: 25 (1944).
59. Jones, H. W., Gall, O. E., and Barnette, R. M., *Fla. Agr. Expt. Sta. Bull.* **298** (1936).
60. Keilm, D., and Mann, T., *Nature* **145**: 145 (1940).
61. Leeper, G. W., *Proc. Roy. Soc. Victoria* **47**: 225 (1935).
62. Leeper, G. W., *Soil Sci.* **63**: 79 (1947).
63. Lott, W. L., *Soil Sci. Soc. Am. Proc.* **3**: 115 (1938).
64. Lutman, B. F., *Vt. Agr. Expt. Sta. Bull.* **196** (1916).
65. Marsh, R. P., and Shive, J. W., *Soil Sci.* **51**: 141 (1941).
66. Maze, P., *Ann. Inst. Pasteur* **28**: 21 (1914).
67. McHargue, J. S., *J. Ind. Eng. Chem.* **18**: 172 (1926).
68. McHargue, J. S., *Soil Sci.* **60**: 115 (1945).
69. McHargue, J. S., and Roy, W. R., *Bot. Gaz.* **94**: 381 (1932).
70. McLarty, H. R., *Sci. Agr.* **16**: 625 (1936).
71. McLean, F. T., and Gilbert, B. E., *Science* **61**: 636 (1925).
73. Midgley, A. R., and Dunklee, D. E., *Soil Sci. Soc. Am. Proc.* **4**: 302 (1939).
74. Moeberg, E. G., and Harding, M. V., *Science* **77**: 510 (1933).
75. Mowry, H., and Camp, A. F., *Fla. Agr. Expt. Sta. Bull.* **273** (1934).
76. Naftel, J. A., *J. Am. Soc. Agron.* **29**: 761 (1937).
76a. Neish, A. C., *Biochem. J.* **33**: 300 (1939).
77. Orth, D. S., Wickwire, G. C., and Burge, W. E., *Science* **79**: 33 (1934).
78. Parker, E. R., Southwick, R. W., and Chapman, H. D., *Calif. Citrograph* **25**: 74 (1940).
79. Parkinson, G. G., and Nelson, J. M., *J. Am. Chem. Soc.* **62**: 1693 (1940).
80. Peech, M., *Soil Sci.* **51**: 473 (1941).
81. Piper, C. S., *J. Aust. Inst. Agr. Sci.* **6**: 162 (1940).
82. Piper, C. S., *J. Agr. Sci.* **32**: 143 (1942).
83. Purvis, E. R., *Soil Sci. Soc. Am. Proc.* **4**: 316 (1939).

84. Purvis, E. R., and Ruprecht, R. W., *Fla. Agr. Expt. Sta. Bull.* **307** (1937).
85. Raulin, J., *Ann. Sci. Comp. rend.* **56**: 229 (1870).
86. Reeve, E., Prince, A. L., and Bear, F. E., *N. J. Agr. Expt. Sta. Bull.* **709** (1944).
87. Riceman, D. S., and Donald, C. M., *J. Dept. Agr. Sci. Aust.* **42**: 959 (1939).
88. Roberts, J. W., and Pierce, L., *Phytopath.* **19**: 106 (1929).
89. Rogers, L. H., Gall, O. E., and Barnette, R. M., *Soil Sci.* **47**: 237 (1939).
90. Rogers, L. H., Gall, O. E., Gaddum, L. W., and Barnette, R. M., *Fla. Agr. Expt. Sta. Bull.* **341** (1939).
91. Rudra, M. N., *Nature* **141**: 203 (1938).
92. Ruehle, G. D., and Lynch, S. J., *Proc. Fla. State Hort. Soc.* **53**: 152 (1940).
93. Schaller, W. T., *U. S. Geol. Survey Prof. Paper* **158** (1930).
94. Scheele, K. W., *Opuscula Chemica et Physics* **1** (1774).
95. Sherman, G. D., *Com. Fert.* **67**, No. 5: 28 (1943).
96. Sherman, G. D., and Harmer, P. M., *Soil Sci. Soc. Am. Proc.* **7**: 398 (1942).
97. Sherman, G. D., McHargue, J. S., and Hegeman, J. S., *Soil Sci.* **56**: 127 (1943).
98. Shive, J. W., *Soil Sci.* **60**: 41 (1945).
99. Sjollema, B., and Hudig, J., *Verslag. Land. Onderzoek Rijksland Expt. Sta. Rec.* **21**: 115 (1909).
100. Skoog, F., *Am. J. Bot.* **27**: 939 (1940).
101. Smith, R. E., and Thomas, R. E., *Phytopath.* **18**: 449 (1928).
102. Sommer, A. L., *Am. Fert.* **72**, No. 6: 15 (1930).
103. Sommer, A. L., *Plant Physiol.* **6**: 339 (1931).
104. Sommer, A. L., *Soil Sci.* **60**: 71 (1945).
105. Sommer, A. L., and Lipman, C. B., *Plant Physiol.* **1**: 231 (1926).
106. Sommers, I. I., and Shive, J. W., *Plant Physiol.* **17**: 582 (1942).
107. Stewart, F. C., French, G. T., and Sirrine, F. A., *N. Y. Agr. Expt. Sta. Bull.* **349** (1912).
108. Swingle, W. T., and Webber, H. J., *U. S. Dept. Agr., Div. Veg. Physiol. Path. Bull.* **8** (1896).
109. Teakle, L. J. H., and Stewart, A. M., *J. Aust. Inst. Agr. Sci.* **5**: 50 (1939).
110. TerMeulen, H., *Nature* **130**: 966 (1932).
111. Townsend, G. R., *Fla. Agr. Expt. Sta. Press Bull.* **487** (1936).
112. Townsend, G. R., *Fla. Agr. Expt. Sta. Press Bull.* **488** (1936).
113. Trumble, H. C., *J. Dept. Agr. S. Aust.* **48**: 445 (1944).
114. Warrington, K., *Ann. Bot.* **37**: 629 (1923).
115. Warrington, K., *Ann. Applied Biol.* **24**: 475 (1937).
116. Whetstone, R. R., Robinson, W. O., and Byers, H. G., *U. S. Dept. Agr., Bur. Plant Ind. Tech. Bull.* **797** (1942).
117. Wild, A. S., and Teakle, L. J. H., *J. Dept. Agr. W. Aust.* **19**: 71 (ser. 2) (1942).
118. Williams, C. B., *Ann. Rept. N. Carolina Agr. Expt. Sta.*, p. 46 (1930).

General References

119. Boron Symposium, *Soil Sci.* **57** (1944).
120. Brenchley, W. E., "Inorganic Plant Poisons and Stimulants." Cambridge, Mass., Cambridge University Press (1927).
121. Dennis, R. W. G., and O'Brien, M. A., *Res. Bull.* 5, *W. Scotland Agr. Coll., Plant Husbandry Dept.* (1937).

122. Hambidge, G., editor, "Hunger Signs in Crops," Washington, D. C., Judd and Detweiler.
123. Hoagland, D. R., "Inorganic Plant Nutrition." Waltham, Mass., Chronica Botanica Co. (1944).
124. Lundegardh, H., *Ann. Rev. Biochem.* **17**: 503 (1947).
125. Minor Element Symposium, *Soil Sci.* **60** (1945).
126. Stiles, W., "Trace Elements in Plants and Animals." New York, The Macmillan Co. (1946).

PART III

NUTRITION OF FARM ANIMALS

Chapter XIII

THE NUTRITION OF DAIRY CATTLE

SEDGWICK E. SMITH

Cornell University, Ithaca, N. Y.

An appreciation of the nutrition of dairy cattle demands an understanding of the processes of a ruminating animal that has been selectively bred, managed, and fed to produce large quantities of milk, primarily for human consumption. The good dairy cow will produce milk year after year using, in addition to grains and grain by-products, large amounts of roughages which are unsuited as a direct source of nutrients for monogastric animals. Morrison[75] has stated "Among all the animals of the farm, dairy cows of good productive capacity are unequalled as producers of human food." In terms of energetic efficiency the cow, producing about 35 pounds of milk per day and properly fed, converts about 33 per cent of the total digestible nutrients in the feed consumed into milk. This energetic efficiency is about twice that of egg production and about five times that of meat production.[13] Both Maynard[62] and Morrison[13] have recently reviewed the question of efficiency of livestock production.

Milk production has been said to be the backbone of American agriculture and milk consumption the keystone of American nutrition. Dairy products rank first among farm products in cash receipts. In 1945 the gross farm income from dairy products totaled $3,632,146,000 as compared to cattle and calves for meat $3,255,386,000; poultry and eggs $3.049,084,000; hogs $2,674,454,000; and vegetables $2,056,371,000. Approximately one-third of the gross income for dairy products was collected by the five leading dairy states which ranked in the order of Wisconsin, New York, California, Minnesota, and Pennsylvania.

Although the dairy industry is gigantic in the aggregate, the average dairy farm is small and typically a single family enterprise. Half of the country's approximately 38 million head of dairy cattle are located in herds of 8 cows or less and three-fourths are in herds of 15 or less.[13] The estimated average annual milk production of the dairy cow in United States is about 5000 pounds. In 1944 the average cow in dairy herd improvement associations produced 8217 pounds of milk at a total feed cost of $119 ($1.45 per 100 pounds of milk) and returned over feed costs a product valued at $167.

The richness of milk in protein, energy, calcium, phosphorus, and vitamin A properly accounts for its title of the "most perfect single food."

Milk is of course not a perfect food. It is notably deficient in iron, copper, manganese, cobalt, and some others. Its high nutritive value combined with its high palatability accounts for the large consumption by the American public. In 1945 the total milk (all milk products) consumption was 799 pounds per capita of which 438 pounds was consumed in the form of fluid milk or cream.

The process of milk production is one of the most demanding forms of production for nutrients. This is easily realized when one considers that a 1200-pound cow which produces 8000 pounds of milk per year secretes an amount of dry matter equivalent to about twice that in her entire body. The output of nutrients in high producing cows is tremenduous; for example in one year Carnation Ormsby Madcap Fayne produced the record 41,943 pounds of milk which in terms of dry matter is equal to about ten times the total dry matter in a 1200-pound cow. There are several cows on record as having produced over 150,000 pounds of milk in a lifetime. In terms of dry matter this is equivalent to about 36 times the dry matter in an average 1200-pound cow. In contrast to these figures a 1000-pound steer furnishes about 500 pounds of edible dry matter, and this, of course, only once.

The large nutrient turnover of milking cows, combined with the known composition of milk, gives some idea of the general nutrient requirements of the milking cow, which are: (1) liberal amounts of energy, (2) a relatively large amount of protein, (3) at least a certain minimum amount of fat, (4) adequate minerals, especially phosphorus and calcium and salt, and (5) an ample supply of vitamins, particularly A and D. The amounts of nutrients will depend on (1) the body size, since maintenance requirements are proportional to body size, (2) the amount of milk produced, and (3) its richness in fat. If the animal is still growing, additional nutrients will be needed for this process. When pregnant, there will be a still further nutrient requirement for the development of the fetus, its membranes, and the mammary glands.

In the space allotted to this subject it is impossible to give more than a summary of existing information. For those desiring greater detail the following publications are especially recommended: (1) "Feeds and Feeding" by Morrison,[73] (2) "Dairy Science" by Petersen,[84] (3) "Animal Nutrition" by Maynard,[61] (4) "Bioenergetics and Growth" by Brody,[13] (5) "Secretion of Milk" by Espe,[30] (6) "The Physiology of Domestic Animals" by Dukes,[20] and (7) "The Nutrition of Calves" by Savage and McCay.[92]

Physiology of the Ruminant Stomach

The ability of cattle to secure a large amount of nutrients from bulky forages is dependent largely on the activities of the ruminant stomach which consists of four compartments—rumen, reticulum, omasum, and abomasum. (See Chapters XIV and XV in Volume I.) The rumen and reticulum together form a large fermentation vat. The feed, hastily swallowed at first, is regurgitated and chewed (rumination), which increases the total surface area exposed to attack; it is stirred by strong muscular contractions of the walls of the stomach in a fluid medium constantly renewed by the inflow of saliva, and is held for a considerable time under anerobic conditions and at a pH favorable to the growth and multiplication of microorganisms. The heat of animals and the heat of fermentation of the mass of feed contribute to establish optimum conditions for microbial activity.

In the mature cow the rumen accounts for about 80 per cent of the total stomach capacity and will contain some 40–60 gallons of material. The rumen is lined with a nonglandular mucous membrane and the epithelium is a stratified squamous type, which type is held to be structurally unsuited for absorption. In spite of this, recent studies have demonstrated that absorption of various compounds can and do occur from the rumen, such as the lower fatty acids, glucose, ascorbic acid, and various drugs.[5, 19, 28] It is primarily in the rumen that the various microorganisms break down certain feed constituents and synthesize other nutrients. The rumen is in direct contact with the reticulum, a much smaller compartment which is thought to function as the rumen but in a smaller way. The omasum, a globe-shaped organ filled with laminae, is situated between the reticulum and the abomasum. One function of the omasum is to grind feed materials that enter it, but knowledge as to the extent of this or how it is done is largely unknown. The abomasum, sometimes called the true stomach, is the glandular portion of the ruminant stomach. It secretes a gastric juice and apparently functions much like the stomach of monogastric animals.

The microorganisms—bacteria, protozoa, and yeast—are present in the rumen in enormous quantities (about 30 per cent of dry matter[45]) and play a large role in the metabolism of feedstuffs in ruminants. Studies so far as they have gone have shown that these organisms catabolize cellulose, synthesize proteins from simple nitrogenous compounds, synthesize many of the B-vitamins and produce quantities of the lower fatty acids, notably acetic, propionic and butyric. These metabolic activities are primarily conducted for the use of the microorganisms, but inasmuch as these organisms are later digested, their nutrient-laden protoplasm becomes available to the animal body, thus sparing or supplementing the nutrients derived directly from ingested feeds. This fascinating subject is still in its infancy. Several recent reviews are available.[4, 45, 55, 66, 85, 86]

NUTRIENT REQUIREMENTS

The nutrient requirements of the dairy cow vary with the age, size, level of milk production, and state of reproduction. In feeding practice the following stages are generally recognized; calves up to 6 months of age; heifers from 6 months up to first calving; milking cows (barn and

TABLE 93. MORRISON FEEDING STANDARDS FOR DAIRY CATTLE

	Digestible protein [Lower amounts, minimum advised. Higher amounts advised under usual conditions] lb.	Total Digestible Nutrients [Lower amounts, minimum advised Higher amounts, advised under usual conditions lb.	Calcium g.	Phosphorus g.	Carotene mg.	Net Energy [Lower amounts, minimum advised. Higher amounts advised under usual conditions] therms
1. Dairy cows						
A. For maintenance per head daily						
Weight of cow in lbs.						
700	0.44 - 0.48	5.1 - 5.8	7.0	7.0	42	4.1 - 4.6
750	0.47 - 0.51	5.4 - 6.2	7.5	7.5	45	4.4 - 4.9
800	0.49 - 0.54	5.8 - 6.5	8.0	8.0	48	4.6 - 5.2
850	0.52 - 0.56	6.1 - 6.9	8.5	8.5	51	4.9 - 5.5
900	0.55 - 0.59	6.4 - 7.2	9.0	9.0	54	5.1 - 5.8
950	0.57 - 0.62	6.7 - 7.6	9.5	9.5	57	5.4 - 6.1
1000	0.60 - 0.65	7.0 - 7.9	10.0	10.0	60	5.6 - 6.3
1050	0.63 - 0.68	7.3 - 8.3	10.5	10.5	63	5.8 - 6.6
1100	0.65 - 0.71	7.6 - 8.6	11.0	11.0	66	6.1 - 6.9
1150	0.68 - 0.73	7.9 - 9.0	11.5	11.5	69	6.3 - 7.2
1200	0.70 - 0.76	8.2 - 9.3	12.0	12.0	72	6.6 - 7.4
1250	0.73 - 0.79	8.5 - 9.6	12.5	12.5	75	6.8 - 7.7
1300	0.75 - 0.82	8.8 - 10.0	13.0	13.0	78	7.0 - 8.0
1350	0.78 - 0.84	9.1 - 10.3	13.5	13.5	81	7.3 - 8.2
1400	0.80 - 0.87	9.4 - 10.6	14.0	14.0	84	7.5 - 8.5
1450	0.83 - 0.90	9.7 - 11.0	14.5	14.5	87	7.7 - 8.8
1500	0.85 - 0.92	10.0 - 11.3	15.0	15.0	90	8.0 - 9.0
1550	0.88 - 0.95	10.2 - 11.6	15.5	15.5	93	8.2 - 9.3
1600	0.90 - 0.98	10.5 - 11.9	16.0	16.0	96	8.4 - 9.6
1650	0.93 - 1.00	10.8 - 12.3	16.5	16.5	99	8.7 - 9.8
1700	0.95 - 1.03	11.1 - 12.6	17.0	17.0	102	8.9 - 10.1
1750	0.98 - 1.06	11.4 - 12.9	17.5	17.5	105	9.1 - 10.3
1800	1.00 - 1.08	11.7 - 13.2	18.0	18.0	108	9.3 - 10.6
B. For milk production per lb. of milk [To be added to allowance for pregnancy.]						
For milk of:						
3.0%	0,036 - 0.043	0.26 - 0.28	1.0	0.75	-	0.24 - 0.26
3.5%	0.038 - 0.046	0.28 - 0.30	1.0	0.75	-	0.26 - 0.28
4.0%	0.041 - 0.049	0.31 - 0.32	1.0	0.75	-	0.29 - 0.30
4.5%	0.044 - 0.052	0.33 - 0.35	1.0	0.75	-	0.31 - 0.32
5.0%	0.046 - 0.056	0.35 - 0.37	1.0	0.75	-	0.33 - 0.35
5.5%	0.049 - 0.059	0.38 - 0.40	1.0	0.75	-	0.35 - 0.37
6.0%	0.052 - 0.062	0.40 - 0.42	1.0	0.75	-	0.37 - 0.39
6.5%	0.054 - 0.065	0.42 - 0.45	1.0	0.75	-	0.39 - 0.41
C. Additional allowance for last 2 to 3 months of pregnancy. [To be added to allowance for main maintenance and allowance for milk produced.]						
Small Cow	0.50 - 0.55	5.0 - 5.5	10.4	6.4	24	0.43 - 0.47
1,000-lb. cow	0.55 - 0.60	5.5 - 6.0	13.0	8.0	30	0.47 - 0.51
Large cow	0.65 - 0.70	6.5 - 7.0	15.6	9.6	36	0.55 - 0.60

TABLE 93—CONTINUED

REQUIREMENTS PER HEAD DAILY

	Dry Matter lb.	Digestible Protein lb.	Total Digestible Nutrients lb.	Calcium g.	Phosphorus g.	Carotene mg.	Net Energy therms
2. Growing Dairy Cattle Weight in lbs.							
60	0.8- 1.1	0.20 - 0.25	1.0 - 1.3	5	4	6	1.2 - 1.6
100	1.6- 2.6	0.30 - 0.40	1.4 - 2.1	8	6	6	1.5 - 2.3
150	3.2- 4.6	0.43 - 0.52	2.5 - 3.5	12	8	9	2.5 - 3.5
200	4.7- 6.4	0.53 - 0.62	3.5 - 4.5	16	11	12	3.3 - 4.5
300	7.2- 9.0	0.67 - 0.77	5.0 - 6.0	18	13	18	4.5 - 5.5
400	9.1-11.4	0.76 - 0.87	6.0 - 7.0	20	15	24	5.4 - 6.3
500	10.7-13.0	0.81 - 0.92	6.9 - 8.1	19	15	30	6.1 - 7.2
600	12.4-14.7	0.84 - 0.95	7.9 - 9.1	18	15	36	7.0 - 8.0
700	14.2-16.5	0.87 - 0.98	8.6 - 9.9	17	15	42	7.4 - 8.5
800	15.9-18.3	0.90 - 1.00	9.2 - 10.6	16	15	48	7.9 - 9.1
900	17.3-19.7	0.93 - 1.03	9.8 - 11.2	16	15	54	8.4 - 9.6
1000	18.6-21.0	0.95 - 1.05	10.3 - 11.7	15	15	60	8.9 - 10.1
3. Mature Dairy Bulls Heavy Service Weight in lbs.							
1200	14.7-16.3	1.02 - 1.12	9.8 - 10.8	12	12	72	8.5 - 9.5
1400	17.2-19.0	1.19 - 1.31	11.0 - 12.2	14	14	84	9.6 - 10.6
1600	18.6-20.6	1.28 - 1.42	12.3 - 13.5	16	16	96	10.7 - 11.9
1800	20.4-22.6	1.40 - 1.54	13.5 - 14.9	18	18	108	11.8 - 13.0
2000	22.0-24.2	1.50 - 1.66	14.8 - 16.4	20	20	120	12.9 - 14.3
2200	24.1-26.7	1.65 - 1.83	16.0 - 17.8	22	22	132	14.1 - 15.5
2400	26.3-29.1	1.80 - 2.00	17.4 - 19.2	24	24	144	15.1 - 16.7
2600	28.5-31.5	1.96 - 2.16	18.5 - 20.5	26	26	156	16.2 - 18.0

pasture feeding), and dry cows which includes the late stages of pregnancy.

Before animals can sustain production, they must first be fed for their essential life processes. The common term used to designate this is maintenance and the feed necessary to meet this fundamental requirement is the maintenance ration which is defined as that amount of feed which will just support the body when doing no work and yielding no products. Such a ration will meet the needs of the body for maintaining its normal temperature, the energy required for activity of the circulatory and respiratory systems and to replace the daily losses of proteins and minerals and the minimum vitamin requirements. The maintenance requirement is a function of body size, although there is disagreement as to quantitative aspects of this.[18]

Growth is a state of high nutrient requirements. The more rapid the rate of growth the higher are the requirements, and as a result rapidly growing animals are more likely to suffer from deficiencies than at other stages of life. The rapid increase in the musculature and other organs demands a high protein intake and, especially in the case of monogastric animals, a protein of proper quality. The developing skeletal system requires a high intake of calcium and phosphorus and other minerals. The adequacy of the ration in iron is important since the blood volume is rapidly increasing. The high activity of young animals and the rapid rate of metabolism demand a high energy and vitamin intake.

Lactation is another productive state of high nutrient requirements—energy, protein, minerals, and vitamins. The nutrient requirements of a lactating cow depend on her body size, amount of milk produced, and the amount of fat in the milk. These are all taken into consideration in sound feeding standards. To meet the nutrient requirements one must, of course, know the size of the animal (direct weighings or estimated weight from measurements of the height and girth[89]), the weight of milk produced, and the fat percentage.

The nutrient requirements of pregnancy are not large—at first only slightly above maintenance requirements and increasing to a significant figure only during the later third of pregnancy. Accurate figures for pregnancy requirements are few, but in terms of energy the average in-

Table 94. National Research Council's Recommended Nutrient Allowances for Dairy Cattle

Weight of Animal lb.	Expected Gain		Daily Allowance per Animal[1]					
	Jersey lb.	Holstein lb.	Digestible Protein lb.	Total Digestible Nutrients lb.	Ca g.	P g.	Carotene mg.	Vitamin D I.U.
Growth: 50	0.5	-	0.30	1.0	4	3	-[2]	150
100	1.0	0.8	0.45	2.0	8	6	6	300
150	1.3	1.4	0.60	3.0	12	8	10	450
200	1.4	1.6	0.70	4.0	13	9	12	600
400	1.2	1.8	0.80	6.5	14	11	25	1200
600	0.8	1.4	0.85	8.5	15	12	35	-
800	1.1	1.2	0.90	10.0	15	12	45	-[3]
1,000	-	1.3	0.95	11.0	14	12	60	-
1,200	-	1.2	1.00	12.0	12	12	70	-
Maintenance:[4] 700			0.45	6.0	7	7	40	-[3]
1,000			0.60	8.0	10	10	60	-
1,200			0.70	9.5	12	12	70	-
1,400			0.80	11.0	14	14	80	-
Pregnancy [per 1,000 lb.] [Last 6 to 12 weeks]			1.20	14.0	22	17	90	-[3]
Lactation [per lb. milk]								
3.0% fat			0.040	0.28	1	0.7	-[5]	-[5]
4.0% fat			0.045	0.32	1	0.7	-	-
5.0% fat			0.050	0.37	1	0.7	-	-
6.0% fat			0.055	0.42	1	0.7	-	-

[1] Thiamine, riboflavin, niacin, pyridoxine, pantothenic acid, and vitamin K are synthesized by bacteria in the rumen and it appears that adequate amounts of these vitamins are furnished by a combination of rumen synthesis and natural feedstuffs. Manganese, iron, copper, and cobalt are clearly essential but the amounts needed are not known. For growth 0.6 g. magnesium is needed per 100 pounds body weight.

[2] Calves should receive colostrum the first few days after birth, as a source of vitamin A and other essential factors.

[3] While vitamin D is known to be required the data are inadequate to warrant specific figures for older growing animals and for maintenance, reproduction, and lactation.

[4] When calculating the allowances for lactating heifers that are still growing, it is recommended that the figure Growth rather than Maintenance be used.

[5] When adequate amounts of vitamins A and D are fed for normal reproduction, extra amounts will probably not stimulate milk production but will increase the vitamin content of the milk.

creased requirement in terms of energy is about 6 per cent over maintenance requirements.[70] In terms of protein the average increase is of the order of 17 per cent.

In the case of the dairy cow the nutrient requirements of various forms of production differ probably only quantitatively rather than qualitatively. A possible exception is the newborn calf, which with its undeveloped rumen may be more sensitive than a mature animal to a dietary deficiency of some of the B-vitamins and amino acids.

Feeding Standards. To guide livestock feeders in selecting balanced rations is the prime purpose of feeding standards. These are tables stating the amounts of certain nutrients which it is believed should be provided to animals for various purposes. Such standards or recommendations rest on experimentally determined data for the nutrients listed, usually plus a factor of safety to allow for variations in animal requirements, composition in feeds, and others. Feeding standards will not be blindly followed by the wise feeder for they are not absolute rules but only approximate guides; also, feeding standards take into account only a limited number of necessary nutrients. For example, the Morrison standards, which are the most widely used in this country, list only digestible protein, total digestible nutrients or net energy, calcium, phosphorus, and carotene. The National Research Council recommended nutrient allowances for dairy cattle lists in addition vitamin D, but not net energy. These standards do not list other important characteristics of a ration such as protein quality, other needed minerals and vitamins, palatabality, general suitability of a feed, and costs. When enough quantitative data are accumulated to permit recommendations regarding these other necessary qualities of a feed they will undobutedly be included in standards.

Morrison's feeding standards and the National Research Council nutrient recommendations for dairy cattle are given in Tables 93 and 94.

Energy. The largest purpose which feed serves the animal body is the production of energy for various body processes. Since all organic nutrients can serve this purpose, energy values provide a common basis for expressing their nutritive value. The fact that these nutrients, especially protein, may have specific functions as well does not alter their common usefulness as sources of energy.

How the energy value of a feed or ration can be expressed most accurately has been a controversial subject for many years and has involved some of the most outstanding physiologists and nutritionists of the world. Unfortunately, in the space allotted to this chapter the problem can only be summarily presented.

The fundamental principle underlying all methods of evaluating feeds on the basis of net available nutrients is the net-energy concept, in accord with which all organic nutrients are measured in terms of calories; and the net available portion of any feed is that portion of the gross energy which remains after the deduction of all energy losses and expenses incident to the process of utilization. It is represented by the simple formula: Net energy = gross energy minus energy of urine, feces, methane, and heat increment. For measuring the productive value of a feed, net energy is the most accurate measure yet proposed. Nevertheless, the use of net-energy values of feeds has many serious disadvantages among which are the expense of securing such data; very few feeds have had their net-energy value determined; the net-energy value is not a constant and varies widely depending on the feed combinations used, the plane of nutrition, the type of production (maintenance, fattening, milk production, etc.); environmental conditions, and others. As a result net-energy values of feeds have been little used in practical livestock feeding. For more detailed discussions of the subject the publications of Kriss,[56] Kleiber,[54] Forbes,[37] and Brody [13] should be consulted.

The limitations of the net-energy system of evaluating feedstuffs make it necessary to use some other system of evaluating feedstuffs for livestock feeding. Modifications of the net-energy, such as starch values and Scandavian feed-units, are used widely in foreign countries. In this country total digestible nutrients are generally used. They are admittedly not as accurate a measure of the productive energy value of feedstuffs as net-energy values but they are easily calculated, and as a result hundreds of feedstuffs have been so evaluated. All that is required is an estimate of the proximate analysis of a feed and an estimate of the digestibility of each class of nutrients. In essence total digestible nutrients (TDN) is the sum of the digestible nitrogen-free extract, digestible crude fiber, digestible protein, and digestible fat, the latter being multiplied by 2.25 to weight its higher energy value. Therefore TDN values of a feed represent an approximate heat or energy value. Feeds low in fiber run high in TDN and vice versa. The cereal grains range in TDN value from about 70–80 pounds per 100 pounds. The hays run from about 45–55 and the straws still lower. A few grains such as flaxseed run over 100 since this seed is so rich in fat. The TDN values of many feeds are compiled in the extensive summaries of Morrison [75] and Schneider.[93]

Lignin, while not a carbohydrate, is conveniently discussed with the carbohydrates. Its chemical structure is uncertain, but it is known to contain carbon, hydrogen, and oxygen. Methoxy groups occur to the extent of about 15 per cent of the molecule. Lignin is digested little if at all by higher animals; thus its presence in feeds is undesirable. Not only is lignin unavailable in itself, but it has been postulated that insofar as it encapsulates other more digestible nutrients it lowers the over-all digestibility of feedstuffs. Some unpublished data of the author [94] indicate furthermore that lignin may have a direct depressing effect on the digestibility of certain nutrients. Since lignin is undigestible it may be used as a reference substance to estimate the digestibility of a feed. This method has the advantage of not requiring quantitative collections of either feed or feces.[24, 97]

Accompanying the fermentation of the carbohydrates there is a nutrient loss in the heat of fermentation and in the combustible gases that are expelled. Some of the heat may be used to keep the animal body warm but any in excess of this is wasted. The methane loss is of the order of 10 per cent of the total digestible nutrients.

Before a mature dairy cow can produce milk, the maintenance energy requirement must be satisfied. To the extent that energy remains after this, milk can be produced. The maintenance energy requirement of cows has been determined in various ways and by several different researchers. For a summary of these studies see Morrison.[75] For a 1000-pound cow the Morrison standard recommends a range of 7.0–7.9 and the National Research Council 8.0 pounds of TDN per head daily. The TDN requirements for milk production depend on the amount of milk produced and its richness in fat. For each pound of 4 per cent-fat milk produced per day the Morrison standard recommends a range of 0.31–0.32 and the National Research Council 0.32 pound of TDN over maintenance needs.

Fat. In addition to its contributions of energy, fat apparently plays a more specific role in the rations of lactating cows. Many experiments have shown that both body fat and milk fat can be made from dietary carbohydrates, but experiments of Maynard and associates[63] have shown that a minimum amount of fat in the ration is necessary for maximum milk production. In a total of 18 experiments, more 4 per cent fat-corrected milk was always produced when the concentrate mixture contained 4–6 per cent fat as compared to mixtures containing about 2 per cent fat. It was calculated from these studies that 100 pounds of grain containing 4 per cent of fat produced as much milk as did 104 pounds of grain with only 2 per cent of fat. Such studies as these are of especial interest in these days when fat is being extracted so efficiently from the grains for human and industrial consumption.

The percentage of fat in milk may be decidedly influenced for short periods of time by feeding the cow certain high-fat feeds as flaxseed, soybeans, peanuts, or certain fats.[75] Coconut oil meal and palm-kernel meal have in some tests temporarily caused a slight increase in the fat percentage. On the other hand, the feeding of cod-liver oil or menhaden fish oil has resulted in a decrease in the fat content of milk.[65]

The character of milk fat may be decidedly changed by feeding certain other feeds. Heavy feeding of cottonseed or cottonseed meal is a cause of hard, crumbly butter due to an increase in the high melting point fats.

Coconut meal also increases the hardness of butter which may become objectionable when more than 3-4 pounds of pressure-process meal is fed per day. On the contrary heavy feeding of soybeans or rice polish may cause an objectionably soft butter.

The controversy over the nutritive merits of oleomargarine and butter is an interesting one but beyond the scope of this summary. Recent reviews of this discussion are given by Cowgill[15] and a report of the National Research Council.[80]

Proteins. The protein requirements of most animals involve both quantitative and qualitative aspects, the latter referring to the presence of the essential amino acids. In monogastric animals quality is as important as quantity, for a decided deficiency of either will lead to poor performance or even death. In the case of dairy animals, as well as other ruminants, the quality of dietary protein is of much less importance. This is because the synthetic activities of the various microorganisms in the digestive tract rework the dietary proteins and other nitrogenous compounds into protein for their own use. As these organisms are later digested by the animal their synthesized proteins become available to the host. An excellent recent review of this subject is given by McNaught and Smith.[66] Although many details are still hidden, enough facts have been found to permit a sketchy outline of these metabolic changes. That the mature ruminant is less sensitive to the quality of dietary protein has been demonstrated many times in feeding trials. For example, linseed meal as the only protein supplement to a ration of grain and hay gives excellent results with dairy cattle. On the other hand, linseed meal fed as the only protein supplement to grain for swine gives poor results. Such a poor quality protein supplement as corn gluten feed, when fed with a ration of ground corn, corn silage, and alfalfa hay, will give excellent results in dairy cattle.[75] The phase of nitrogen metabolism which has been given most attention, however, is the conversion of nonprotein nitrogen, especially urea, to protein in the rumen. McNaught and Smith have summarized these findings and the following statements are taken from this review. Bacteria in the rumen degrade the dietary protein and urea, some of it to ammonia, and synthesize protein from ammonia. The deliberate use of nonprotein nitrogen compounds is successful only when the available feedstuffs are rich in starch and poor in protein. The readily available carbohydrate is required apparently as a source of energy for the bacteria. The protozoa of the rumen do not appear to be active in the nitrogen cycle, but their protein derived in turn from the ingested bacteria may be more easily digested by the host. Since part of the dietary protein as well as the nonprotein nitrogen present is converted into bacterial protein in the rumen, and since bacterial protein has a high nutritive value, biological values as determined for nonruminants are of little significance for maintenance and growth in the ruminant. Thus to the ruminant the quality of dietary protein is of little importance—the bacteria of the digestive tract rework it so thoroughly that it matters little what the source of nitrogen has been because the host eventually receives a uniform quality of protein of high nutritive value.

It has been shown conclusively that simple nitrogenous compounds as urea can serve as a source of protein to ruminants, but most workers have found that such compounds are not as effective a source of nitrogen as its nitrogen equivalent in the form of natural proteins for either growth,[41, 59] nitrogen balance,[40] or lactation.[104] The reasons for this difference are unknown. It appears rather unlikely that nonprotein nitrogenous compounds will serve as an important source of protein to ruminants under normal economic conditions. In times of severe protein deficiency such simple compounds might well be used as protein extenders.

Although mature dairy cattle are not demanding in the quality of dietary protein, the same may not hold true for the newborn calf with its undeveloped rumen and lack of a normal complement of flora and fauna. Pounden and Hibbs[87] in studies of the rate of development of the flora and fauna of the rumen of the calf have shown that not until the calf is about 90 days of age do the majority have flora and fauna normally found in the mature cow. Just how sensitive the calf is to quality of dietary protein and at what age this assumed sensitivity changes are still unknown. In practical feeding it is usually recommended that feeds containing protein of high quality be fed, such as milk or milk by-products, the better quality plant proteins, and animal by-products.

The protein requirements of a mature dairy cow for body maintenance have been studied by many investigators who for the most part have shown this requirement to be about 0.6 pound digestible crude protein for a 1000-pound cow.[75] The Morrison standards recommend a range of 0.60–0.65 pound of digestible protein per day for a 1000-pound cow. The National Research Council recommendation is 0.6 pound. Data as to the protein requirements of pregnancy in the cow are meager, but those available indicate a pregnancy requirement over maintenance requirements of about 17 per cent for the period of pregnancy. This figure rises significantly to a maximum of about 40 per cent at the end of gestation. This added protein is required for growth of the fetus, its membranes, the uterus, and the mammary gland. For growth, a period of high protein needs, much more data are needed to establish the protein requirements. The Morrison standards and the National Research Council recommendations have been previously given.

Vitamin A. The chemistry and physiology of the various inorganic elements and vitamins have been dealt with in Chapters XX and XXI of Volume I, and, in order to prevent unnecessary duplication, general discussions of these substances will not be given here. Rather, aspects of these nutrients which have specific applications to dairy cattle will be emphasized.

Of the known vitamins, only A and D have been shown to be limiting in rations ordinarily fed to dairy cattle. By use of a ''synthetic milk'' dairy calves have been shown to require riboflavin, thiamine, and biotin. A dietary need of the other vitamins remains to be demonstrated.

Vitamin A is essential for all animals so far studied. In the case of dairy cattle and other herbiverous animals their usual feeds contain little or none of it. This riddle was subsequently resolved by the finding that carotene and other carotenoids can be converted to vitamin A by animals, chiefly in the intestinal wall. Efficiency of conversion varies with species, the rat being a highly efficient converter and the cow a poor converter, much of the dietary carotene being stored in the body fat as such.[74] Furthermore, breeds of cattle differ in the proportion of carotene stored and converted which accounts for the difference in the depth of color of the body and milk fat of the Jersey and Guernsey breeds on the one hand and the other dairy breeds on the other hand.

The symptoms of vitamin A deficiency in cattle have been extensively studied.[38a] Recent reviews of these studies have been made by Hart,[44] and Duncan and Huffman.[49]

Among the organs specifically affected by a lack of vitamin A is the eye. In the case of cattle this is manifested by night blindness, papillary edema, lachrymation, clouding of the cornea, keratitis, ulceration, and permanent blindness. The peramanent blindness appears to be due to a stenosis of the optic canal as a result of bone overgrowth. This mechanically constricts the optic nerve, causing its degeneration.[71] In addition to the eye, metaplasia of many epithelia of the body occurs. Inadequate vitamin A interferes with reproduction in both sexes. In the male the germinal epithelium is destroyed and consequently spermatogenesis is reduced or stopped altogether. Such sterility is not permanent and on refeeding vitamin A normal spermatogenesis may be resumed.[27] In the cow a lack of vitamin A does not interfere with conception but it does result in marked placental injury so that such females give birth to premature dead or weak and blind calves. Another important symptom of this avitaminosis is a rise in the spinal fluid pressure due presumably to an overgrowth of the bony encasement of the central nervous system.[73] More recently Madsen [60] has emphasized the occurrence of edema of the legs and brisket in vitamin A deficient cattle and the occurrence of cystic degeneration of the pituitary gland.

Of practical importance is the ability of cattle to store large amounts of vitamin A and/or carotene during periods of luxury consumption.

Enough may be stored to adequately meet the needs of the animal for many months even though the dietary intake during this time is nil.

The vitamin A value of milk is a function of the amount of carotene or the vitamin itself in the ration. During periods of vitamin A deficiency, the content of the milk may be so low that calves fed exclusively on it will develop deficiency symptoms. At times of large intakes of carotene, as on pasture, the milk is a rich source of vitamin A value. Winter milk (March) according to a recent study contained 1060 I.U. of vitamin A per quart as compared to 2005 I.U. for summer milk (September) produced by cows on pasture.[18] A recent comprehensive survey of the vitamin A potency of butter produced in the United States has been made.[2] The weighted averages for summer and winter butter was 17,955 and 11,160 I.U. per pound, respectively.

Under usual conditions cattle, except suckling calves, derive their vitamin A from carotene in plants and plant products, particularly pasturage, well-cured hay, and corn and hay-crop silages. Of the common grains only yellow corn furnishes any significant amount of carotene, and this is not large.

The minimum requirement of vitamin A for cattle has been determined by Guilbert et al.[39] to be 5.1–6.4 micrograms per kilogram of body weight per day. In terms of carotene the requirement was established at 43–55 I.U. Other workers using different criteria of vitamin A adequacy have set higher figures.[39, 58] For feeding practice much higher amounts than these are, of course, recommended and these have been previously given.

Vitamin D. The amount of vitamin D required for normal bone calcification varies with the amounts and ratio of calcium and phosphorus in the ration as well as with the species concerned. Apparently the calf requires vitamin D per se in addition to adequate calcium and phosphorus.[6] The studies of Wallis [101] have shown that even the mature cow needs some vitamin D, although in order to demonstrate this experimental rations containing beet pulp as the only roughage were used.

In view of the intense metabolism of calcium and phosphorus in lactating cows it might be expected that vitamin D would play a large role in milk secretion, but apparently this is not true. In the studies of Wallis, a vitamin D deficiency did not develop in lactating cows until all hay was replaced by molasses-beet pulp in a ration otherwise devoid of the vitamin. The large losses of calcium and phosphorus which occur in liberally producing cows are not prevented by large intakes of vitamin D.[43] Apparently this vitamin is not readily secreted into the milk and, in terms of the needs of young animals, milk is not a potent source of it. Massive doses of vitamin D will increase the content in milk, but the inefficiency of this process has led to the use of other means of enriching milk such as direct additions of the vitamin or irradiation. Normal milk has a vitamin D potency of about 5–44 U.S.P. units per quart, being highest in the summer and lowest in the winter. There is a close correlation between the vitamin D potency and the hours of exposure to sunshine, indicating that sunlight is the principal factor involved in these variations.[14]

The common sources of vitamin D available to cattle are sunshine and sun-cured roughages. Artificially cured roughages run lower in this vitamin than sun-cured roughages. The studies of Huffman[48] have shown that 2 pounds a day of sun-cured hay permits the normal development of calves in so far as vitamin D is concerned.

The vitamin D recommendations for growing calves of Morrison's standards and the National Research Council have been cited previously. Insufficient data exist to permit a recommendation for mature lactation animals.

For the symptoms of rickets, see the discussion of calcium and phosphorus.

Vitamins B, C, E, and K. More than thirty years ago Theiler,[99] who observed that ruminants could be maintained for long periods of time on a ration very low in certain vitamins, mentioned that it was at least possible that the vitamin needs could be covered indirectly by bacterial synthesis in the intestine. Since that time several different workers have confirmed this hypothesis. It now appears established that the following vitamins are produced in the rumen by microbial activity: vitamin K, biotin, folic acid, niacin, pantothenic acid, pyridoxine, and riboflavin. The evidence for thiamine synthesis is not conclusive, although it has been shown that an exogenous source of thiamine is not required by ruminants.[55] A few observations have been reported that the rumen synthesis of at least some of the B-vitamins is influenced by the nature of the ration, especially the kind of carbohydrate present, but quantitatively significant data are difficult to obtain with the techniques so far used. Because of the known synthesis of the B-vitamins it is commonly assumed that no account need be taken of these vitamins in rations but direct proof is lacking that this assumption always hold true.

It has been pointed out by many that in the case of the calf, until the normal microbial population becomes established in the rumen, there may be a dietary requirement of some of the B-vitamins. Recent reports[51, 102, 103] bear this out. The Illinois workers by use of a "synthetic milk" in which various nutrients could be varied at will have observed biotin, thiamine, and riboflavin deficiency in calves. Attempts to produce a niacin deficiency in calves were unsuccessful.[52] The studies of Lundquist and Phillips indicating a beneficial effect on calf scours by niacin and vitamin-A therapy have not been confirmed by a recent large-scale study of Spielman et al.[95]

Although the ruminant is known not to require a dietary supply of ascorbic acid, the site of its synthesis is unknown. It appears that the rumen is not the site of synthesis, but the recent paper of Erb et al.[29] showing that ascorbic acid is rapidly absorbed from the rumen indicates the possible inadequacies of past techniques which depended so largely on observing an increased concentration of these nutrients in the rumen. The early studies[85] indicating that ascorbic acid is a valuable therapeutic agent in treating sterility in cattle have not generally been accepted.

According to Gullickson et al.,[39a] vitamin E is required by cattle, but is not specifically needed for reproduction. Claims have been made that this vitamin is useful in the prevention and cure of sterility. Such claims are without valid foundation. The recent report that vitamin E supplementation results in increased fat production in lactating cows[42] needs confirmation, especially since the cost of such supplementation is a significant item.

The hemorrhagic disease resulting from the ingestion of spoiled sweet clover high in dicumarol is known to be a vitamin K antagonism. As such, vitamin K therapy of sweet clover disease should prove effective as it has shown to be in laboratory animals.[1]

Minerals. The 13 or possibly 14 (fluorine) required minerals do not all constitute a practical problem on the farm inasmuch as ordinary feeds supply more than enough of most of these for dairy animals. A few other minerals, such as selenium, fluorine, and molybdenum, constitute a feeding problem in that they are highly toxic. In the following discussion most attention will be given to those minerals that are likely or may occasionally be limiting in farm-type rations.

Salt. Most of the feedstuffs fed to cattle are deficient in salt (sodium chloride). Therefore, salt supplementation is a generally recommended practice. Salt may be added to the concentrate mixture at a level of 1 per cent. This is generally done in most commercial mixtures. In addition, it is advisable to allow cattle free access to salt in either the block or flake form in a box protected from the weather.

Few recent studies have been made of the salt requirements of dairy cattle or of its functions in the body. The early work of Babcock[3] still stands out as one of the most extensive studies. It was here reported that cows deprived of salt exhibited an abnormal appetite for it after two or three weeks. In no case, however, did the health of the animal, as shown by appearance, milk production, or live weight, appear to be affected until after much longer periods of privation. This period of immunity varied from 1 month with some cows to over a year with others. Eventually, however, every cow reached a condition of sudden breakdown from which recovery was rapid when salt was fed. The general deficiency symptoms were loss of appetite, a general haggard appearance, lusterless eyes, rough coat, and a very rapid decline in body weight and milk yield. The breakdown was most likely to occur at calving or immediately thereafter. Those cows producing large amounts of milk were most quickly affected which would be expected, since large amounts of salt are secreted in the milk.

Babcock by calculations came to the assumption that about 0.75 ounce of salt per day was the minimum requirement per 1000 pounds of weight. For milk production the requirement was calculated to be about 0.3 ounce of salt for each 10 pounds of milk produced. It was recommended that dairy cows be given at least 1 ounce of salt per head daily. Cows allowed salt free-choice will consume up to about 3–4 ounces per head daily.

It is still an unanswered question whether the salt requirement is primarily a sodium or a chlorine requirement or both. In this respect an observation of Babcock's is worthy of note. Potassium chloride was given to one cow in a state of collapse and this cow recovered as quickly and as completely as cows given sodium chloride, which suggests that chlorine may be the primary deficiency.

Phosphorus and Calcium. It is not only convenient but necessary to discuss phosphorus, calcium, and vitamin D together, inasmuch as bone development and growth involve all three to such a large extent, and because the adequacy of the intake of any one is dependent on the intake of the other two. Generally speaking a deficiency of any one of these or a wide ratio of calcium to phosphorus will lead, in the young animal, to the condition termed rickets. In dairy calves, however, rickets almost always is due to a deficiency of phosphorus. This observation is at least partly explained by the relatively high calcium content of most forages and the relative resistance of cattle to a simple calcium deficiency.[67] Calves that receive any reasonable amount of sun-cured hay or sunshine will secure adequate amounts of vitamin D. In calves rickets is revealed in a decreased rate of growth, stiffness of gait, enlarged and painful joints, arching of the back and, as an extreme symptom, the birth of weak or deformed calves.

In older animals a deficiency of phosphorus in the ration leads to the condition called "aphosphorosis" identified by Theiler[98] as osteomalacia. It is usually associated with the intake of phosphorus-low forages as in grazing animals or those fed poor quality winter maintenance rations.[35] Uncomplicated aphosphorosis is characterized by retarded growth, abnormal skeletal development with bone fragility, lameness, poor fertility, depraved appetite, and ultimately complete collapse and death. In either rickets or aphosphorosis, the condition is cured by supplying the missing nutrient. Recovery may or may not be complete. If the deficiency has been of long duration the skeletal architecture may not be completely restored to normal.

Since about 80 per cent of the phosphorus is found in the skeletal system and since milk is rich in this mineral it means that growing, pregnant, and lactating animals have the highest requirements. If a milking cow is fed a concentrate mixture containing about 20 per cent of the high-phosphorus feeds as wheat bran, middlings, or the various oil meals, the phosphorus needs will be met. Most commercial concentrates have added phosphorus supplements in addition to some of the above and thus are rich in phosphorus. Cattle being fed exclusively on forages including pastures or on forages and home-grown grains may require phosphorus supplementation. Any safe supplement as feeding-grade bone meal, dicalcium phosphate, or a properly defluorinated (less than 0.1% fluorine) rock phosphate is a source of both calcium and phosphorus. Adding 1 per cent of any of these to the grain or providing it free-choice in a mineral box should take care of these needs adequately. Space will not permit a discussion of the effect of soil amendments on the phosphorus and other mineral contents of plants but a recent review covers this in detail.[9] A cooperative study of the availability of various phosphorus supplements has been reported.[25]

Extensive experiments have shown the rather surprising fact that even when high-producing cows are fed ideal rations, rich in calcium and phosphorus, they frequently secrete more of these minerals into their milk at the height of milk production than they can assimilate from their feed. During this period they, therefore, draw on the stores of these minerals in their skeletons. When they are producing less milk and especially when they are dry, they are able to rebuild their stores of calcium and phosphorus. It is, therefore, important to supply plenty of these minerals during the dry period.

To find whether the process of drawing on the mineral reserves during high milk production was injurious, continuous metabolism experiments over entire lactation periods have been conducted with good dairy cows.[23, 34] The cows, which yielded 9000 to 15,000 pounds of milk a year, lost calcium and phosphorus during the first part of the lactation period, when their yields were largest. However, in nearly all cases they stored sufficient of these minerals later so that by the next calving time the losses were more than replaced. Adding bone meal, ground limestone, or a mixture of the two tended to lessen the losses of minerals during the early part of the lactation period and to result in a greater storage for the entire year. There was, however, no proof that the addition of these supplements improved the health or production of the cows.

Mitchell[68] has estimated the calcium and phosphorus requirements of dairy animals which are given in Table 95.

Magnesium. The distribution and metabolism of magnesium are closely associated with calcium and phosphorus. Approximately 70 per cent is located in the bones. Particularly due to the studies of Huffman et al.[21] with calves our attention has been focused on the problem of possible deficiencies in dairy animals. These workers have shown that calves on milk rations develop a tetany characterized by low blood magnesium levels but normal levels of calcium and phosphorus. Bone calcification is impaired and frequently there is calcification of the soft tissues. A similarity exists between these symptoms and the disease called "grass tetany." This disease is a form of tetany characterized by a low blood magnesium level and has been reported in many parts of the world. It is also called "lactation tetany" because it occurs most often, but not exclusively, in lactating cows when they are turned to pasture in the spring. Such an attack is frequently fatal. The low blood magnesium level and the fact that animals respond favorably to injections of magnesium salts have led to the belief that the ailment is due primarily to a low magnesium intake, although chemical analyses of the feeds does not support the theory of a magnesium deficiency.[91] More studies are obviously indicated.

TABLE 95. CALCIUM AND PHOSPHORUS REQUIREMENTS OF GROWING HOLSTEIN HEIFERS, EXPRESSED AS PERCENTAGES OF THE DRY RATIONS

Body Weight lb.	Age mos.	Ca Required %	Phosphorus Required %	Ca:P Ratio
150	2.2	0.85	0.52	1.6
200	3.0	0.77	0.48	1.6
400	6.6	0.42	0.28	1.5
600	10.6	0.32	0.22	1.4
800	15.4	0.24	0.17	1.4
1000	21.3	0.18	0.14	1.3
1200	28.9	0.18	0.13	1.4

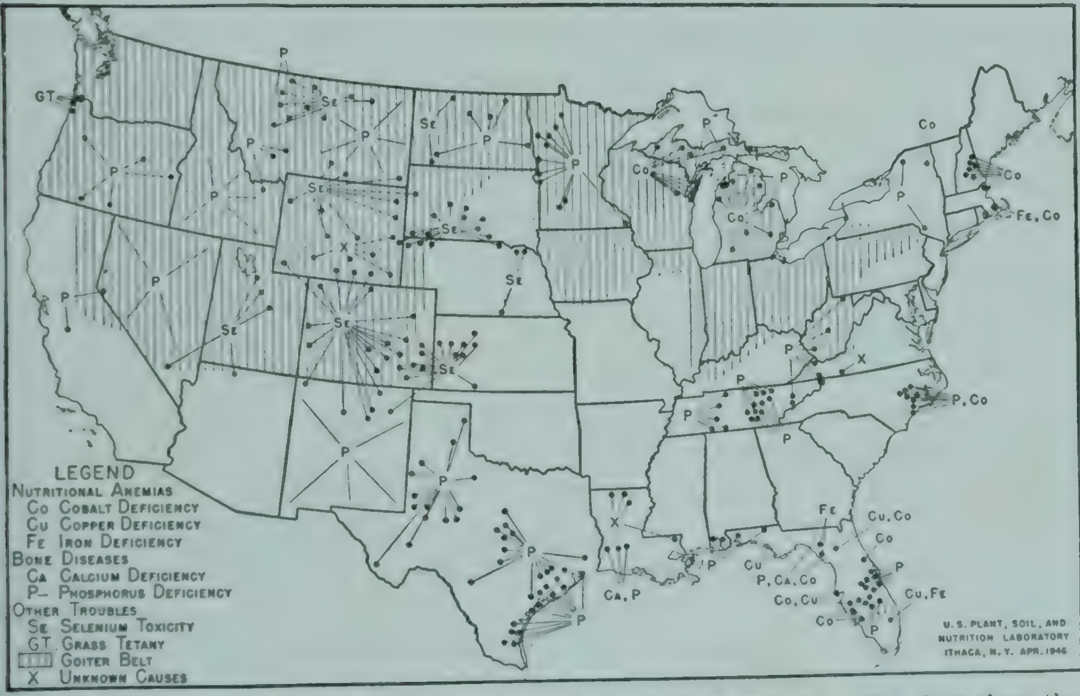
[1] The recommendations of the Morrison standards and the National Research Council are found in Tables 93 and 94.

On the basis of the studies of Huffman et al.[50] the magnesium requirements have been set at 0.6 g. per 100 pounds of body weight which corresponds to about 0.06 per cent of the dry ration. Since most feeds contain at least 0.1 per cent of magnesium, it appears that deficiencies of this element under practical conditions are rare.

Micronutrient Elements. The nutrition and physiology of the micronutrient elements or so-called trace elements—cobalt, iodine, manganese, zinc, and copper—are a rapidly expanding field. The general subject is discussed in Chapter XX, Volume I. Some of these elements become feeding problems in that the soils of certain regions are deficient in available amounts of the minerals and, therefore, the plants grown thereon fail to supply adequate amounts to grazing animals. Strictly speaking iron is not a micronutrient element but is conveniently discussed at this point. Several excellent reviews of these elements are available.[26, 91, 100]

Beeson [10] has compiled a map showing the areas of micronutrient element deficiencies so far reported in livestock in this country, which is given in Figure 28.

A dietary deficiency of iron will lead eventually to an anemia, in the dairy calf as well as in other animals. From time to time there have been reports of iron deficiency areas, but to date none of these reports rest on valid data. In some areas it has been subsequently shown that some element other than iron was primarily involved. Milk, of course, is very deficient in iron as well as some other elements, but the calf is born with a reserve store of iron which is sufficient to carry it through the period of exclusive milk feeding. As soon as other feeds are introduced, the iron requirements are met and thus a "milk anemia" in practice is rare and is of little or no practical concern.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Ca, P
LEGEND
Nutritional Anemias
Co Cobalt Deficiency
Cu Copper Deficiency
Fe Iron Deficiency
Bone Diseases
Ca Calcium Deficiency
P– Phosphorus Deficiency
Other Troubles
Se Selenium Toxicity
GT Grass Tetany
▥ Goiter Belt
X Unknown Causes
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FIG. 28. Occurrence of mineral nutritional diseases in animals. The dots show the approximate location of the observed deficiency. The lines not terminating in dots indicate a generalized area where specific locations have not been reported. The goiter region is also a generalized area.

Dietary deficiencies of zinc and manganese have not yet been clearly demonstrated in dairy cattle.

Iodine. An iodine deficiency causes goiter in calves as well as in other animals. The large area of iodine deficiency in this country is indicated in the map of Figure 28. Before the use of iodized salt in these regions goiterous calves and adults were not infrequently observed, but since that time goiter has rarely been seen. While the exact iodine requirements of calves are unknown, the amount furnished in iodized salt (0.007 per cent of iodine) suffices to prevent a deficiency. Mitchell[68] has estimated the iodine requirement of calves to be 0.09 p.p.m. of the dry ration.

Iodine need not be fed every day when it is required as a supplement because the thyroid gland has considerable ability to store this element. To prevent the birth of weak, dead, or goiterous calves an iodine supply during the later part of pregnancy is particularly important. Iodine in salt is readily lost through sublimation due to the catalytic action of impurities present, unless a stabilizing agent is added.

In nongoiterous areas, negative results have generally followed the administration of iodine supplements to livestock; thus Forbes et al.[36] in Pennsylvania found no beneficial effects on growth of dairy cattle, lambs, chickens, or in the incidence of abortion in cattle or on egg production in poultry. This combined with the fact that overdosage with iodine is a real possibility dictates against any large-scale or excessive iodine supplementation of livestock.

Cobalt. Cobalt, the latest addition to the list of required minerals, was first shown to be essential for animals by two independent groups of Australian workers. The observation of several cobalt deficient areas in this country has stimulated considerable interest in this element and its physiological role. Such deficiency areas have now been reported in Florida, North Carolina, Michigan, Wisconsin, New Hampshire, and probably New York.

Observations to date indicate that cobalt is required by ruminants but not by monogastric animals.[64] These observations combined with some preliminary reports that cobalt injected was ineffective have led to the theory that cobalt functions in some way through the microorganisms of the rumen. Recent work of the Cornell group[37a] showing that cobalt-deficient sheep have a significantly altered flora of the rumen supports this theory.

Symptoms so far noted in cobalt deficient animals are nonspecific and may easily be confused with symptoms due to other causes—anorexia, often an anemia, and decreased production. Such animals respond in a matter of 1–3 weeks when fed a cobalt salt. A favorable response following the feeding of cobalt salts under controlled conditions is the best way at the moment to diagnose a cobalt deficiency.

Information as to requirements is scanty. The Australian workers have reported that cattle grazing forages which contain less than 0.04 p.p.m. of cobalt are likely to be deficient; whereas, if the forage contains above 0.04 p.p.m., the cobalt intake is adequate.[91] This would roughly be equivalent to an intake per day of 0.5 mg. of cobalt per cow. When indicated, cobalt supplementation may be made in a number of ways—fertilizing the soil with 1–2 pounds of cobalt salts per acre; giving the salt as a drench, in the concentrate mixture or in a salt mixture. As a drench, 1 teaspoonful per day of a solution of 1 ounce of cobalt sulfate is adequate. In the concentrate mixture, 2–4 g. of cobalt sulfate per ton or adding about 0.5 ounce of the cobalt salt per 100 pounds of salt or salt-bonemeal mixture should insure an adequate intake.

Cobalt is toxic when fed in excessive amounts. For dairy cattle the tolerance has been reported to be somewhat in excess of 50 mg. of cobalt per 100 pounds of body weight,[53] an amount considerably in excess of requirements.

It has been reported that cobalt therapy is effective in treating ketosis,[46] but the evidence is not convincing. There is no good evidence that cobalt supplementation is helpful in treating sterility of dairy animals.

Copper. The pioneer work of the Wisconsin workers in showing that copper was essential for hemoglobin formation in rabbits and rats has been confirmed in a number of species including dairy cattle. How copper functions in this respect is still unknown.

From the standpoint of livestock feeding copper is similar to cobalt in that it constitutes an area problem in several parts of the world including some sections of Florida in this country.[91]

Among livestock copper deficiency has been studied more thoroughly in sheep than in cattle. In Australia a condition locally termed “falling disease” has been shown to be due to a lack of copper. The predominant symptom is sudden death of cattle in good flesh. This is thought due to lesions of the heart musculature. Preliminary reports[16] from Florida indicate that the disease called “pacing disease,” so-called because cattle pace, is a copper deficiency symptom. This symptom indicates lesions in the nervous system. Nerve lesions due to a lack of copper have been well established in lambs.[33]

Data as to copper requirements of cattle are very meager. In Australia the disease has been observed in cattle grazing forages which contain less than about 5 p.p.m. of copper. This roughly is equivalent to a daily intake of about 15 mg. of the element.

Copper salts, particularly when fed over long periods of time, can be toxic.[11] This combined with the fact that few areas of copper deficiency have been established in this country renders any widespread or excessive copper supplementation of livestock unwise.

Toxic Minerals. Selenium has been found to be responsible for the disease commonly called “alkali disease” or “blind staggers” which is known to exist in many parts of the world, including this country. The symptoms of this toxicity are extensive, including—loss of hair, lameness, and sloughing of the hoofs, anemia, liver damage, and eventually death. The trouble arises from the uptake by plants of this element from soils naturally high in it. Certain plants thrive on seleniferous soils and are thus “indicator or marker” plants. Chronic toxicity has been reported in rations containing 500–1000 p.p.m. Although small amounts of arsenic counteract selenium toxicity, therapeutic measures are practically infective. There seems to be no solution to this problem but to abandon these areas. An excellent review of this problem is given by Moxon and Rhian.[78]

Another highly toxic element which often constitutes a practical problem is fluorine. From the standpoint of dairy cattle feeding this is primarily due to the high fluorine content of rock phosphates used as a phosphorus supplement. Rock phosphate contains about 3.5–4.0 per cent of fluorine; and, even when included in the ration at a level of 1 per cent, this furnishes enough fluorine to exceed the recommended level by about tenfold. The National Research Council report recommends a tentative safe level for cattle of 0.003 per cent of the element in the total ration.[69] This report is also an excellent general review of the fluorine problem. Several methods have been developed to defluorinate rock phosphates and, when properly done, produce a safe product.

One of the interesting recent discoveries in the field of micronutrient elements involves the scouring of cattle on the so-called "teart" pastures in England and the therapeutic effect of copper salts. In continuing their earlier studies, Ferguson et al.,[32] Lewis,[57] and Ferguson[31] observed the high molybedenum content of "teart" pasturage and were able to duplicate the symptoms displayed by cattle on such forage by feeding molybdenum salts. It was further shown that copper sulphate given as a drench prevented and cured the symptoms. More recently Britton et al.[12] have shown that a similar molybdenum toxic area is present in California. The symptoms observed in cattle and the preventive effect of copper confirm the findings of the English workers. Further evidence of a molybdenum-copper interaction has been given by Dick et al.,[17] who observed that molybdenum fed to sheep and cattle results in a reduction of the copper content of the liver even when additional copper was fed. It would thus appear that a high intake of molybdenum in ruminants precipitates a copper deficiency which is prevented and cured by the feeding of additional copper.

Nutrition of the Calf

The nutrition of the calf requires special attention due primarily, but not exclusively, to its undeveloped rumen and its supply of microorganisms. As a result of this the calf must be more sensitive to the quality of the dietary protein; it cannot digest efficiently large amounts of roughage and under certain conditions may develop a deficiency of some of the B-vitamins. The calf is one species born with a deficit of antibodies and, unless this supply is augmented soon after birth, the calf is susceptible to various infections. Colostrum is the most efficient source of these antibodies. Attention has recently been focused on the importance of the reserve supply of vitamins in the newborn calf and its modification by the nutrients fed the pregnant cow.

The importance of colostrum in the nutrition of the young was recognized long ago,[92] but only recently have some of the unique properties of this secretion been appreciated. One of the most important properties is the passive immunity given to calves against many organisms to which calves are very susceptible when fed no colostrum. This property of colostrum is associated with its high content of globulin (6–12 per cent vs. 0.03 per cent for milk). The rise of agglutinins in calf blood is positively correlated with the rise of globulins.[82] Calves deprived of colostrum suffer a high mortality,[47] which emphasizes the importance of feeding colostrum regardless of the system subsequently followed in raising calves. For more details of this subject the reader is referred to several review articles.[28, 88]

Another important feature of colostrum, which has not received the attention it deserves, is the high nutrient content as compared to milk.

TABLE 96. A COMPARISON OF THE COMPOSITION OF COLOSTRUM AND MILK *

	Colostrum	Milk
Total solids	24.72	12.78
Ash	1.37	0.75
Protein	13.97	2.92
Fat	8.45	4.33
Lactose	3.63	4.78
Ca	0.256	0.130
Mg	0.037	0.011
K	0.137	0.153
Na	0.074	0.036
P	0.235	0.113
Fe	2.00	0.11 - 0.65 mg./kg.
Cu	0.56	0.09 - 0.30 mg./kg.
Co	0.005	
Carotene	4.73	0.41 mg./l
Vitamin A	2.4	0.40 mg./l
Vitamin D	1.22	0.41 I. U./g. fat
Thiamine	0.62	0.38 γ/ml.
Riboflavin	6.10	1.77 γ/ml.
Pantothenic acid	2.24	3.67 γ/ml.
Niacin	0.96	0.91 γ/ml.
Tocopherol	107.00	16 γ/g. fat

* Figures extracted from various publications.

The full importance of this in supplying the meager nutrient reserves of calves at birth is not yet clear, but sufficient studies have been made to indicate that such contributions are not to be ignored. A comparison of the composition of colostrum and milk is given in Table 96. That colostrum composition may be varied by feeding the dam has been shown for vitamin A and vitamin D.[22, 96]

The lack of a full complement of symbiotic organisms in the calf stomach has been referred to previously. In the newborn calf the rumen and reticulum together make up only about one-third of the volume of the entire stomach. The mature proportions of the stomach are not established until the cow is about a year and a half old, at which time the rumen makes up about 80 per cent of the total volume, the reticulum 5 per cent, the omasum 7–8 per cent, and the abomasum 7–8 per cent. The time at which a normal microflora is established is in doubt. Pounden and Hibbs[57] have supplied some estimates of this by observing that microorganisms characteristic of the mature cow were present in 33 per cent of calves studied at 30 days of age and were not present in 14 per cent of the calves at 90 days of age. Becker et al.[7, 8] have reported some studies which show that the source of these organisms is the oral secretions of other cattle.

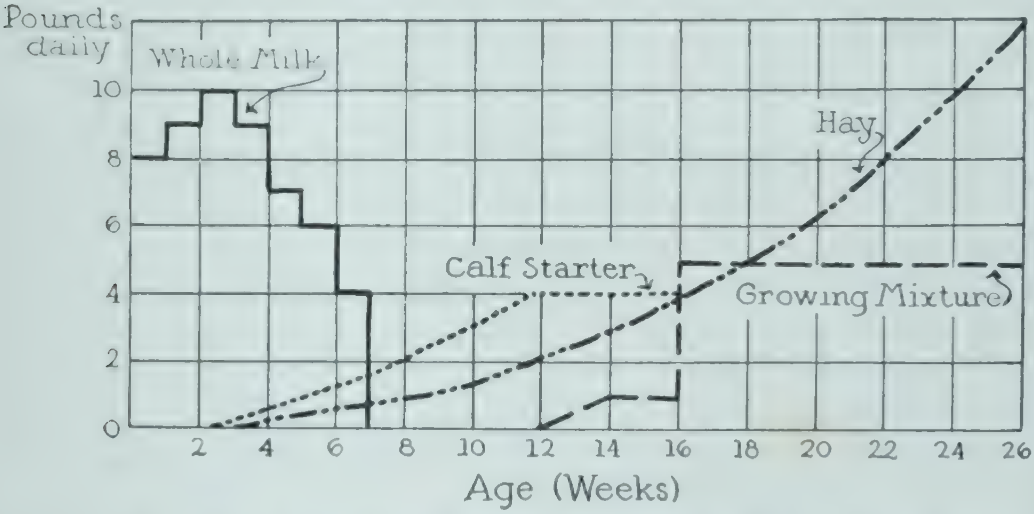

FIG. 29. Feeding schedule for Holstein, Brown Swiss and Ayrshire calves according to the Cornell dry-calf-starter method.

That the young calf is dependent on a dietary supply of some of the B-vitamins has been shown by the Illinois workers who, by use of synthetic milk, have developed and described deficiencies of biotin, thiamine, and riboflavin in calves.[51, 102, 103] By use of the same technique a deficiency of niacin could not be demonstrated.[52] However, in practice where any of the ordinary feedstuffs are used, a deficiency of the B-vitamins has not been reported and apparently is not a feeding problem of major consequences.

The large requirements of the rapidly growing calf for energy, protein, calcium, phosphorus, and vitamin A are adequately met by milk. When maximum development is desired, regardless of the cost, there is no better method of feeding calves than the so-called whole milk method—milk is fed until an age of 6 or more months, grain and hay being introduced at about 2–3 weeks of age. However, the high value of milk for human consumption has stimulated a search for other methods of calf raising in which a minimum amount of milk is used—the so-called dry-calf-starter method.[81] One such method is presented in graphical form in Figure 29. By this method considerable milk is saved for human use and calves can still be grown to compare very favorably with those fed much larger amounts of milk.

BIBLIOGRAPHY

1. Anonymous, *Nutr. Revs.* **3**: 55 (1945).
2. Anonymous, *U. S. Dept. Agr. Misc. Pub.* **571** (1945).
3. Babcock, S. M., *Wisc. Agr. Expt. Sta. Ann. Rept.* **1905**: 129.
4. Baker, F., and Harriss, S. T., *Nutr. Absts. Revs.* **17**: 1 (1947–48).
5. Barcroft, J., McAnally, R. A., and Phillipson, A. T., *J. Expt. Biol.* **20**: 120 (1944).
6. Bechdel, S. I., Helston, N. W., Guerrant, N. B., and Dutcher, R. A., *Pa. Agr. Expt. Sta. Bull.* **364** (1938).
7. Becker, E. R., *Quart. Rev. Biol.* **7**: 282 (1932).
8. Becker, E. R., and Hsiung, T. S., *Proc. Nat. Acad. Sci.* **15**: 684 (1929).
9. Beeson, K. C., *Bot. Rev.* **12**: 424 (1946).
10. Beeson, K. C., *Soil Sci.* **60**: 9 (1945).
11. Boughton, I. B., and Hardy, W. T., *Texas Agr. Expt. Sta. Bull.* **499** (1934).
12. Britton, J. W., and Goss, H. J., *J. Am. Vet. Med. Assoc.* **58**: 176 (1946).
13. Brody, S., "Bioenergetics and Growth." New York, Reinhold Publishing Corp. (1945).
14. Campion, J. E., Henry, K. M., Kon, S. K., and Mackintosh, J., *Biochem. J.* **31**: 81 (1937).
15. Cowgill, G. R., *Physiol. Revs.* **25**: 664 (1945)
16. Davis, G. K., Private communication.
17. Dick, A. T., and Bull, L. B., *Aust. Vet. J.* **21**: 70 (1945).
18. Dornbush, A. C., Peterson, W. H., and Olson, F. R., *J. Am. Med. Assoc.* **114**: 1748 (1940).
19. Dukes, H. H., *J. Expt. Biol.* **20**: 120 (1947).
20. Dukes, H. H., "The Physiology of Domestic Animals." Ithaca, New York, Comstock Publishing Co. (1947).
21. Duncan, C. W., Huffman, C. F., and Robinson, C. S., *J. Biol. Chem.* **108**: 35 (1935).
22. Eaton, H. D., Spielman, A. A., Loosli, J. K., Thomas, J. W., Norton, C. L., and Turk, K. L., *J. Dairy Sci.* **30**: 787 (1947).
23. Ellenberger, H. B., Newlander, J. A., and Jones, C. H., *Vt. Agr. Expt. Sta. Bull.* **331** (1931); **342** (1932); **360** (1933); **380** (1934); **396** (1935).

24. Ellis, G. H., Matrone, G., and Maynard, L. A., *J. Animal Sci.* **5**: 285 (1946).
25. Ellis, N. R., Cabell, C. A., Elmslie, W. P., Fraps, G. S., Phillips, P. H., and Williams, Dorothy E., *J. Assoc. Off. Agr. Chem.* **28**: 129 (1945).
26. Elvehjem, C. A., *Physiol. Rev.* **15**: 471 (1935).
27. Erb, R. E., Andrews, F. N., Hauge, S. M., and King, W. A., *J. Dairy Sci.* **30**: 687 (1947).
28. Erb, R. E., Andrews, F. N., and Nichols, R. E., *J. Dairy Sci.* **30**: 647 (1947).
29. Erb, R. E., Andrews, F. N., and Nichols, R. E., *J. Dairy Sci.* **30**: 649; 673 (1947).
30. Espe, D., "Secretion of Milk." Ames, Iowa, Iowa State College Press (1946).
31. Ferguson, W. S., *Proc. Nutr. Soc.* **1**: 215 (1944).
32. Ferguson, W. S., Lewis, A. H., and Watson, L. J., *J. Agr. Sci.* **33**: 44 (1943).
33. Follis, R. H., "The Pathology of Nutritional Disease." Springfield, Ill., C. C. Thomas.
34. Forbes, E. B., with collaboration of Black, Alex, Braman, Winfred W., Frear, Donald E. H., Kahlenberg, Orme J., McClure, Frank J., Swift, Raymond W., and Voris, LeRoy, *Pa. Agr. Expt. Sta. Bull.* **319** (1935).
35. Forbes, E. B., and Johnson, S. R., *Pa. Agr. Expt. Sta. Bull.* **371** (1939).
36. Forbes, E. B., Kearns, Geo. M., Bechdel, S. I., Williams, P. S., Keith, T. B., Callinbach, E. W., and Murphy, R. R., *J. Agr. Research* **45**: 111 (1932).
37. Forbes, E. B., and Voors, L., *Ann. Rev. Physiol.* **5**: 105 (1943).

37a. Gall, L. S., Smith, S. E., Becker, D. E., Stark, C. N., and Loosli, J. K., *Science* **109**: 468 (1949).

38. Gamble, J. A., Earle, I. P., and Howe, P. E., *U. S. Dept. Agr. Tech. Bull.* **661** (1938).

38a. Goodwin, T. W., and Gregory, R. A., *Biochem. J.* **43**: 505 (1948).

39. Guilbert, H. R., Howell, C. E., and Hart, G. H., *J. Nutr.* **19**: 91 (1940).

39a. Gullickson, T. W., Palmer, L. S., Boyd, W. L., Nelson, J. W., Olson, F. C., Calverley, C. E., and Boyer, P. D., *J. Dairy Sci.,* **32**: 495 (1949).

40. Harris, L. E., and Mitchell, H. H., *J. Nutr.* **22**: 167 (1941).
41. Harris, L. E., Work, S. H., and Henke, L. A., *J. Animal Sci.* **2**: 328 (1943).
42. Harris, P. L., Swanson, W. J., and Hickman, K. C. O., *J. Nutr.* **33**: 411 (1947).
43. Hart, E. B., Steenback, H., Kline, O. L., and Humphrey, G. C., *J. Biol. Chem.* **86**: 145 (1930).
44. Hart, G., *Nutr. Absts. Revs.* **10**: 261 (1940–41).
45. Hastings, E. G., *Bact. Revs.* **8**: 235 (1944).
46. Henderson, J. A., *Cornell Vet.* **37**: 292 (1947).
47. Herman, H. A., *Mo. Agr. Expt. Sta. Bull.* **377** (1937).
48. Huffman, C. F., *Mich. Quart. Bull.* **14** (1931).
49. Huffman, C. F., and Duncan, C. W., *Ann. Rev. Biochem.* **13**: 467 (1944).
50. Huffman, C. F., Conley, C. L., Lightfoot, C. C., and Duncan, C. W., *J. Nutr.* **22**: 609 (1941).
51. Johnson, B. C., Hamilton, T. S., Nevens, W. B., and Boley, L. E., *J. Nutr.* **35**: 137 (1948).
52. Johnson, B. C., Wiese, A. C., Mitchell, H. H., and Nevens, W. B., *J. Biol. Chem.* **167**: 729 (1947).
53. Keener, H. A., Percival, G. P., and Morrow, K. S., *J. Dairy Sci.* **30**: 557 (1947).
54. Kleiber, M., *Nutr. Absts. Revs.* **15**: 207 (1945).
55. Kon, S. K., and Porter, J. W. G., *Nutr. Absts. Revs.* **17**: 31 (1947–48).

56. Kriss, M., *J. Animal Sci.* **2**: 63 (1943).
57. Lewis, A. H., *J. Agr. Sci.* **33**: 52, 58 (1943).
58. Lewis, J. M., and Wilson, L. T., *J. Nutr.* **30**: 467 (1945).
59. Loosli, J. K., and McCay, C. M., *J. Nutr.* **25**: 197 (1943).
60. Madsen, L. L., and Earle, I. P., *J. Nutr.* **34**: 603 (1947).
61. Maynard, L. A., "Animal Nutrition." New York, McGraw-Hill Book Co., Inc. (1947).
62. Maynard, L. A., *J. Nutr.* **32**: 345 (1946).
63. Maynard, L. A., Loosli, J. K., and McCay, C. M., *Cornell Agr. Expt. Sta. Bull.* **753** (1941).
64. Maynard, L. A., and Smith, S. E., *Ann. Rev. Biochem.* **16**: 273 (1947).
65. McCay, C. M., and Maynard, L. A., *J. Biol. Chem.* **109**: 29 (1935).
66. McNaught, M. L., and Smith, J. A. B., *Nutr. Absts. Revs.* **17**: 18 (1947–48).
67. Meigs, E. B., Kane, E. A., and Shinn, L. A., *J. Agr. Research* **51**: 1 (1935).
68. Mitchell, H. H., *J. Animal Sci.* **6**: 365 (1947).
69. Mitchell, H. H., Natl. Res. Council Reprint and Circ. Ser. **113** (1942).
70. Mitchell, H. H., Carroll, W. E., Hamilton, T. S., and Hunt, G. E., *Ill. Agr. Expt. Sta. Bull.* **375** (1931).
71. Moore, L. A., *J. Nutr.* **17**: 443 (1939).
72. Moore, L. A., Berry, M. H., and Sykes, J. R., *J. Nutr.* **26**: 649 (1943).
73. Moore, L. A., and Sykes, J. F., *Am. J. Physiol.* **134**: 436 (1941).
74. Moore, T., *Biochem. J.* **26**: 1 (1932).
75. Morrison, F. B., "Feeds and Feeding." Ithaca, New York, Morrison Publishing Co. (1936).
76. Morrison, F. B., "Feeds and Feeding." Ithaca, New York, Morrison Publishing Co. (1948).
77. Morrison, F. B., *Chronica Botan.* **11**: 247 (1948).
78. Moxon, A. L., and Rhean, M., *Physiol. Revs.* **23**: 305 (1943).
79. National Research Council, "Recommended Nutrient Allowances for Dairy Cattle" (1945).
80. National Research Council Reprint and Circ. Ser. **118** (1943).
81. Norton, C. L., and Eaton, H. D., *Cornell Agr. Expt. Sta. Bull.* **835** (1946).
82. Orcutt, M. L., and Howe, P. E., *J. Expt. Med.* **36**: 291 (1922).
83. Owen, E. C., *Proc. Nutr. Soc.* **5**: 186 (1947).
84. Petersen, W. E., "Dairy Science." New York, J. B. Lippincott Co. (1939).
85. Phillips, P. H., Lardy, H. A., Boyer, P. D., and Werner, G. M., *J. Dairy Sci.* **24**: 153 (1941).
86. Phillipson, A. T., *Nutr. Absts. Revs.* **17**: 12 (1947–48).
87. Pounden, W. D., and Hibbs, J. W., *J. Dairy Sci.* **30**: 582 (1947).
88. Ragsdale, A. C., and Brady, S., *J. Dairy Sci.* **6**: 137 (1923).
89. Ragsdale, A. C., and Brady, S., *Mo. Agr. Expt. Sta. Bull.* **354** (1935).
91. Russell, F. C., *Imp. Bur. Animal Nutr. Tech. Communication* **15**: 69 (1944).
92. Savage, E. S., and McCay, C. M., "The Nutrition of Calves"; a Review. *J. Dairy Sci.* **35**: 595 (1942).
93. Schneider, B. H., "Feeds of the World." *W. Va. Agr. Expt. Sta.*, Morgantown, W. Va.
94. Smith, S. E., Unpublished data.
95. Spielman, A. A., Dalrymple, D. B. H., Norton, C. L., Loosli, J. K., and Turk, K. L., *Am. J. Vet. Res.* **9**: 26 (1948).
96. Spielman, A. A., Thomas, J. W., Loosli, J. K., Whiting, F., Norton, C. L., and Turk, K. L., *J. Dairy Sci.* **30**: 343 (1947).

97. Swift, R. W., Thacker, E. J., Black, A., Bratzler, J. W., and James, W. H., *J. Animal Sci.* **6**: 432 (1947).
98. Theiler, A., *Vet. J.* **90**: 143 (1934).
99. Theiler, A., Green, H. H., and Viljoen, P. R., *Union S. Africa Dept. Agr.*, 3rd and 4th Repts. (1915).
100. Underwood, E. J., *Nutr. Absts. Revs.* **9**: 515 (1939–40).
101. Wallis, G. C., *S. Dakota Agr. Expt. Sta. Bull.* 372 (1944).
102. Wiese, A. C., Johnson, B. C., and Nevens, W. B., *Proc. Soc. Expt. Biol. Med.* **63**: 521 (1946).
103. Wiese, A. C., Johnson, B. C., Mitchell, H. H., and Nevens, W. B., *J. Nutr.* **33**: 263 (1947).
104. Willett, E. L., Henke, L. A., and Maruyama, C., *J. Dairy Sci.* **29**: 629 (1946).

Chapter XIV

THE NUTRITION OF BEEF CATTLE

H. R. Guilbert

University of California, Davis, California

The principal function of the beef cattle industry in producing wealth and promoting human welfare is to harvest and convert into useful products not only the pastures, field clean-up, and roughages of farms and ranches, but also to convert a large part of the annual forage crop from vast areas of range, forest, and desert lands.

Specialized beef production is practiced in North and South America, Great Britain, South Africa, Australia, and New Zealand. Elsewhere production of beef is more largely a by-product of dairying and the salvaging of draft animals. India has the largest cattle population of any country, but little of this great potential food supply is utilized by the people.

In the United States the surplus of grains produced in the corn belt states, augmented by barley and grain sorghums of other regions and the by-products of the cotton, flax, sugar, and milling industries, supports a large feed-lot fattening industry. Although the magnitude of this phase of beef production is great and it is important and necessary in specialized production of high quality beef, finished at an early age, it is responsible for only a small proportion of the total tonnage annually produced. Large numbers of cattle which have received little or no concentrates are marketed directly from pastures and ranges. Those that are grain-fed have already attained 50 to 90 per cent of their final weight before going into feed lots. Furthermore, 30 to 60 per cent of feed-lot rations commonly is composed of roughages. Swine and poultry are dependent largely on concentrates, and dairy cattle generally utilize concentrates in addition to roughage throughout productive life. Thus, beef cattle and sheep compete much less than other farm animals for primary foods or for lands that may be used directly for growing human food crops.

This background of beef production is presented to emphasize the relative concern of the beef cattle industry with the chemical events, processes, and changes in composition of plants from early stages of growth until maturity as affected by soil, temperature, moisture, and other environmental factors. These environmental factors not only govern the botanical composition of the forage and the nutritive value as affected by the chemical characteristics of the species but also affect, within limits, the chemical composition of the individual species as well.

The higher protein and calcium content of legumes compared with the lower content of these constituents in grasses, particularly at later stages of maturity, is an example of species variation. Soils, deficient in certain mineral elements, produce mineral-poor plants. Phosphorus deficiency occurs over wide areas of the world particularly in semi-arid and arid regions. Phosphorus commonly, and sulfur sometimes are limiting factors for growth of legumes. Correction of the deficiency may lead to a very favorable chain of events. Increase of legumes enhances soil nitrogen which subsequently may stimulate not only greater production of grasses and other nonlegume forage, but also alter them favorably from the standpoint of nutritive value.

Solution of beef cattle nutrition problems involves, on the one hand, cataloging the quantitative nutrient requirements for growth, fattening, reproduction, and lactation, and, on the other hand, the accumulation of knowledge of composition and availability of these nutrients in the feed supply. On the basis of these supply and demand data, the correction of deficits and excesses may be undertaken intelligently by means of supplemental feeding, feed combinations, fertilization, or other cultural and management practices.

Correction of deficits inherent in the feed supply or which occur seasonally by reason of maturing of range forage, increases efficiency of reproduction, promotes continuous normal growth and development, permits faster and more extensive improvements through breeding, and produces more meat of higher quality from the available feed supply through greater over-all efficiency.

Space limitation will not permit treatment of the voluminous literature on feed composition and digestibility. Certain aspects of these subjects have been discussed in Chapters XIV and XV in Volume I. References to some of the more important researches and compilations are given at the end of this chapter. The discussion which follows summarizes briefly some of the characteristics of ruminant nutrition and presents data on quantitative nutritional requirements for practical beef production.

SOME PECULIARITIES OF RUMINANT NUTRITION

Peculiarities of ruminant nutrition were reviewed by Goss [15] in 1942, and have been considered at some length in the previous chapter in this volume. Herbivora have in the alimentary canal a large compartment where the bulky, fibrous material of their diet can be held to soak and to ferment. In such animals as the horse and rabbit the caecum and enlarged colon perform these functions and possibly have some advantages by being located posteriorly in the digestive tract. Readily fermentable starches and sugars are largely digested and assimilated before reaching the caecum and thus avoid energy losses incident to fermentation. The celluloses which are not broken down by enzymatic digestion are then acted upon by the microflora and fauna and in part are rendered available to the host animal largely in the form of organic acids. In ruminants the stomach is partitioned into four compartments. In the adult the first section or rumen is especially large to hold a great bulk of fibrous food. In the young calf the first three compartments are small compared with the fourth or true stomach. In the course of a few weeks, however, with the inclusion of grains and roughages in the diet, the rumen increases remarkably in relative size, reaching a more or less constant relationship to the true stomach at the age of a year to a year and a half.[29, 37] Because of these changes there are marked differences in the nutrition of the young ruminant compared with adult. The nutrition of the young calf has been reviewed by Savage and McCay.[36] Not only are young calves unable to handle bulky feeds, but also they are more dependent directly upon the food supply for essential nutrients which later are synthesized by rumen microorganisms.

As the rumen enlarges, numerous species of bacteria and infusoria become established there and assume a remarkable symbiotic relationship with the host.

Ruminants have no incisors in the upper jaw. In cattle preliminary mastication is incomplete. Heavier seeds and grains tend to drop into the reticulum—largely by-passing the rumen—and since comparatively small amounts of grains are returned in the regurgitated bolus for remastication, whole grains may pass almost unchanged through the digestive tract.

Cattle secrete enormous amounts of saliva which contains no ptyalin and has little or no action on starches.[10] Colin [9] estimated from experiments with salivary fistulae that a steer secretes 50 to 60 kg. of saliva in 24 hours, containing 300 g. of $NaHCO_3$. By this means, the fatty acids produced by bacterial fermentation are neutralized—the salivary secretion being adjusted to maintain a favorable environment for the microorganisms at a pH of 7 or a little less.

The importance of rumen digestion in rendering available energy from cellulose and other complex polysaccharides has long been recognized. Since the thorough study of rumen physiology by Schalk and Amadon [37] much progress has been made, but the quantitative study of the extent of rumen digestion is extremely difficult. The rumen secretes no enzymes, and the products formed are not necessarily ready for absorption. The end result is, however, analogous to digestion even though fermentation rather than enzymatic hydrolysis is the principal reaction. The products of fermentation are mostly organic acids. According to Elsden and co-workers,[12] the average proportion is 67 per cent acetic, 19 per cent propionic and 14 per cent butyric. These workers isolated nearly

400 g. of volatile acid from the rumen and reticulum of an ox. On the basis of these data, the indication of fairly rapid absorption rates, and other indirect evidence, it appears that a significant proportion of energy requirement may be met by these sources.

Synthesis of Nutrients in the Rumen. The difference between ruminants and nonruminants in the nutrients that must be supplied in the food is largely due to microbiological synthesis of essential compounds in the rumen and subsequent digestion of the organisms or assimilation of the free nutrients from the substrate. For this digestion and assimilation, the location of the storage and fermentation compartments in the fore of the digestive tract would appear to be a distinct advantage over the caecum and colon.

From the knowledge that microorganisms could use inorganic N in their metabolism it was early suggested [41, 46] that the microorganisms of the rumen might synthesize protein. The relatively good biological value of the proteins from microbes cultured from rumen contents was established by experiments with dogs and rats.[23, 35] It is now firmly established that the addition of nonprotein nitrogen compounds such as urea to a protein-poor ration will promote growth. From a practical viewpoint such supplementation is more suitable for maintenance and moderate growth than for maximum growth and fattening. For these purposes 25 to 40 per cent of the protein may be obtained from nonprotein nitrogen.[3, 14, 21, 22, 43] For more complete references to the literature consult the reviews by Krebs [28] and by Goss.[15]

Extensive experiments involving rations low or devoid of the vitamin-B complex, but otherwise adequate, and analyses of rumen contents, milk and excreta, have revealed the synthesis by microorganisms of thiamine, riboflavin, pyridoxin, pantothenic acid, nicotinic acid, and biotin. Similarly evidence was obtained for synthesis of fat soluble vitamin K.[5, 30, 31, 32, 42, 43] Ascorbic acid apparently is synthesized through the normal metabolic processes of cattle. No evidence of microbiological synthesis has been obtained, and none is required in the ration, but it is found in the tissues and milk.

When cattle have rations adequate in other nutrients, they are not susceptible to deficiencies of nutrients in the feed which the microorganisms are capable of synthesizing. The rate of synthesis, is, however, dependent on the substrate. The rate of thiamine and riboflavin production is enhanced by the presence of readily fermentable carbohydrates such as molasses. Moreover, the dominance of the types of organisms varies with the feed supply—a diet high in cellulose favors the cellulose-splitting organisms. Micro-species vary in nutrient requirement and ability to synthesize different entities. Available evidence indicates that not all these nutrients may be supplied to the host in adequate amounts under all conditions. Indeed, the study of the nutrition of cattle cannot well be separated from the nutrition of the microflora and fauna with which they are symbiotically associated. For example, one cannot readily explain the digestible protein requirement for fattening 2-year-old steers upon the basis of the increment in the live-weight gain, the proportion of feed protein that can be converted and the requirement for maintenance. The amount so calculated is too low to support maximum food consumption and gain. Is the additional protein essential to maintenance of the most favorable flora in the intestinal tract? Further research is needed on these questions.

Rumen Gas Production and Bloat. Large volumes of gases are produced from rumen fermentation. According to Kleiber, Cole and Mead,[26] who essentially confirmed earlier analysis, the composition of rumen gas from cows on alfalfa pasture was 67 per cent CO_2; 26 per cent CH_4; 7 per cent $N_2 + H_2$; 0.1 per cent H_2S; and less than 1 per cent O_2. These authors report an average production of 180 liters of CO_2 per day from dry cows fed a maintenance ration; 280 liters per day from lactating cows fed production rations. To expel this large volume of gas, eructation is a normal and absolutely necessary process in ruminants. Bloat in ruminants has recently been reviewed by Cole, Huffman, Kleiber, Olson, and Schalk.[7]

Carbon dioxide may be produced by microorganisms from almost unlimited number of organic substances. The rapid gas production during the first 90 minutes following ingestion of food is derived largely from sugars; starches and cellulose may produce as much CO_2 per gram as does sugar, but they require longer fermentation time. Since saliva contains bicarbonates corresponding to an equivalent of 200 volumes per cent CO_2, the daily secretion may transport an equivalent of 120 liters of CO_2 to the rumen. The acidity of the rumen contents determines whether or not CO_2 evolves from the bicarbonates.

According to Woodman and Stewart,[45] methane production is not an integral part of cellulose digestion, but rather a side reaction involving the sugar resulting from decomposition of cellulose. Methane may also arise from ingestion of glucose [25,27] and be derived from bacterial reduction of CO_2. Van Neil [41] has reviewed the knowledge of chemosynthetic CO_2 reduction by various organisms. According to his theory this may be represented by the equation,

$$4\ H_2A + CO_2 \rightarrow CH_4 + 2\ H_2O$$

in which A represents any organic or inorganic hydrogen acceptor.

Although many factors doubtless contribute to the amount and rate of gas produced, the rate is roughly proportional to the amount of feed

TABLE 97. RECOMMENDED NUTRITIVE ALLOWANCES FOR BEEF CATTLE. (All feeds or rations are calculated on the basis of 90 per cent dry matter)

Body Weight lb.	Expected Daily Gain lb.	Daily Feed		Digestible Nutrients		Digestible Protein		Calcium		Phosphorus		Carotene Daily per Animal mg.[1]
		% of Live Weight	Per Animal lb.	% in Ration	Daily per Animal lb.	% in Ration	Daily per Animal lb.	% in Ration	Daily per Animal g.	% in Ration	Daily per Animal g.	
Normal growth, heifers and steers												
400	1.6	3.0	12	58	7.0	7.5	0.9	0.37	20	0.28	15	25
600	1.4	2.7	16	53	8.5	5.7	0.9	0.25	18	0.21	15	35
800	1.2	2.4	19	50	9.5	4.7	0.9	0.19	16	0.17	15	45
1,000	1.0	2.1	21	50	10.5	4.3	0.9	0.16	15	0.16	15	55
Bull, growth and maintenance [moderate activity]												
600	2.3	2.7	16	63	10.0	8.1	1.3	0.33	24	0.25	18	35
800	1.7	2.3	18	61	11.0	7.8	1.4	0.28	23	0.22	18	45
1,000	1.6	2.2	22	55	12.0	6.4	1.4	0.22	22	0.18	18	55
1,200	1.4	2.0	24	54	13.0	6.0	1.4	0.19	21	0.17	18	65
1,400	1.0	1.9	26	54	14.0	5.4	1.4	0.17	20	0.15	18	75
1,600	....	1.7	26	54	14.0	5.4	1.4	0.15	18	0.15	18	90
1,800	...	1.6	26	54	14.0	5.4	1.4	0.15	18	0.15	18	100
Wintering weanling calves												
400	1.0	2.8	11	55	6.0	6.4	0.7	0.32	16	0.24	12	25
500	1.0	2.6	13	54	7.0	6.2	0.8	0.27	16	0.20	12	30
600	1.0	2.5	15	53	8.0	5.3	0.8	0.24	16	0.18	12	35
Wintering yearling cattle												
600	1.0	2.7	16	50	8.0	5.0	0.8	0.22	16	0.17	12	35
700	1.0	2.4	17	50	8.5	4.7	0.8	0.21	16	0.16	12	40
800	0.7	2.3	18	50	9.0	4.5	0.8	0.20	16	0.15	12	45
900	0.5	2.0	18	50	9.0	4.5	0.8	0.20	16	0.15	12	50
Wintering pregnant heifers [weights are for beginning of winter period, gains, average for period]												
700	1.5	2.9	20	50	10.0	4.5	0.9	0.20	18	0.18	16	55
800	1.3	2.3	20	50	10.0	4.5	0.9	0.20	18	0.18	16	55
900	0.8	2.0	18	50	9.0	4.5	0.8	0.20	16	0.18	15	55
1,000	0.5	1.8	18	50	9.0	4.5	0.8	0.20	16	0.18	15	55
Wintering mature pregnant cows [weights are for beginning of winter period gains, average for period]												
800	1.5	2.8	22	50	11.0	4.5	1.0	0.20	22	0.18	18	55
900	1.0	2.2	20	50	10.0	4.5	0.9	0.20	18	0.18	16	55
1,000	0.4	1.8	18	50	9.0	4.5	0.9	0.20	16	0.18	15	55
1,100	0.2	1.6	18	50	9.0	4.5	0.8	0.20	16	0.18	15	60
1,200	0.0	1.5	18	50	9.0	4.5	0.8	0.20	16	0.18	15	65
Cows nursing calves, first 3 to 4 months after parturition												
900-1,100	None	....	28	50	14.0	5.0	1.4	0.24	30	0.18	24	300
Fattening calves finished as short yearlings												
400	Average for period, 2.0 pounds daily	3.0	12	67	8.0	9.2	1.1	0.37	20	0.28	15	25
500		2.8	14	68	9.5	8.6	1.2	0.31	20	0.25	16	30
600		2.7	16	68	11.0	8.1	1.3	0.28	20	0.23	17	35
700		2.6	18	68	12.0	7.8	1.4	0.25	20	0.22	18	40
800		2.5	20	68	13.5	7.5	1.5	0.22	20	0.20	18	45
900		2.3	21	68	14.5	7.2	1.5	0.21	20	0.19	18	50
Fattening yearling cattle												
600	Average for period, 2.2 pounds daily	3.0	18	65	11.5	7.2	1.3	0.25	20	0.21	17	35
700		3.0	21	65	13.5	7.0	1.4	0.21	20	0.19	18	40
800		2.8	22	65	14.0	6.8	1.5	0.20	20	0.19	19	45
900		2.7	24	65	15.5	6.7	1.6	0.18	20	0.18	20	50
1,000		2.6	26	65	17.0	6.5	1.7	0.17	20	0.17	20	55
1,100		2.4	27	65	17.5	6.3	1.7	0.16	20	0.16	20	60
Fattening two-year-old cattle												
800	Average for period, 2.4 pounds daily	3.0	24	62	15.0	6.3	1.5	0.18	20	0.18	20	45
900		2.9	26	62	16.0	6.3	1.6	0.17	20	0.17	20	50
1,000		2.7	27	62	17.0	6.3	1.7	0.16	20	0.16	20	55
1,100		2.6	29	62	18.0	6.3	1.8	0.15	20	0.15	20	60
1,200		2.4	29	62	18.0	6.3	1.8	0.15	20	0.15	20	65

[1] See footnote, page 381.

eaten, and no consistent or significant difference appears from feeds that produce bloat and those that do not. The rate was the same, for example, from fresh green alfalfa as from equivalent amount of dried hay.

The numerous theories regarding the cause of acute bloat are discussed in the review cited above. The "lack of coarse roughage" theory, advanced by Cole and co-workers,[7, 8] appears most generally tenable under a wide variety of conditions. It is predicated upon the conclusive evidence of Schalk and Amadon[37] that rumination and eructation depend upon stimulation of nerve fibers in the rumen by coarse roughage; that the eructation is a reflex rather than a voluntary act. Chemical, as well as physical, stimulation may be involved, but the fact remains that finely ground roughage or cellulose in the form of paper pulp does not promote normal rumen function and the tendency to bloat is increased in animals so fed. Rapid consumption of large quantities of lush immature legumes is most conducive to bloat. Acute bloat from grasses is rare, probably because rapid consumption is more difficult and because most grasses have leaves with rough or scabrous surfaces which are effective in eliciting the eructation response.

QUANTITATIVE NUTRIENT REQUIREMENTS

The data on nutritional requirements of beef cattle recently have been evaluated and summarized by a sub-committee on beef cattle and published as a report of the Committee on Animal Nutrition of the National Research Council.[17] The recommended allowances were calculated to meet various practical production objectives for growth, wintering, reproduction, lactation, and growth and fattening.

The basis of arriving at the recommended allowances is given in some detail in the publication cited above. Energy metabolism experiments, slaughter experiments, and mineral and nitrogen balance trials with a broad supporting base of group trials and practical production experiments and records constitute the foundation for the recommendations.

The recommended allowances for total daily feed, digestible nutrients, digestible protein, calcium, phosphorus, and carotene together with expected daily gain are presented in Table 97.

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[1] The recommended carotene allowances for fattening animals is at the same rate as for cattle in other classifications because this is about the minimum rate that will result in significant storage and thus assure contribution of vitamin A value for human use from the beef liver and fat. For optimum growth or feed-lot gains, and freedom from clinical symptoms, 1.5 mg. carotene for each 100 lb. body weight suffices for cattle previously depleted of body stores; and, when economically necessary, this level may be used except for pregnant or lactating cows. The vitamin A value of the liver and the body fat of animals so fed, however, would be practically nil. Actually, no dietary carotene or vitamin A is needed so long as the animals have sufficient storage reserve to meet physiological needs.

Source of data: Guilbert, H. R., and Paul Gerlaugh, and L. L. Madsen. "Recommended Nutrient Allowances for Beef Cattle." A report of the Committee on Animal Nutrition of the National Research Council. 32 p. Washington, D. C. (1945.)

Requirements are expressed both in percentage of the ration and in daily amounts per animal. Except for the limited rations used for wintering cattle the figures under "Daily Feed, Per Cent of Live Weight" and "Daily Feed per Animal" closely represent the feed capacity of beef cattle at various ages, weights, and degrees of fatness. Feed intake is limited on the one hand by the bulk-handling capacity of the intestinal tract, on the other by the digestible nutrient storage capacity of the animals. The fattening allowances are in general calculated to meet the digestible nutrient storage capacity and to utilize the full feed capacity of the animals and hence represent about the maximum utilization of roughage compatible with optimum gain and rapid fattening. To meet the requirements for normal rumen function and bloat prevention, the recommended minimum roughage allowance was tentatively set at 0.7 to 0.8 pound per 100 pounds live weight; some trouble is apt to occur at about 0.5 pound per 100 pounds live weight.

The expected gain and recommended allowances for wintering cows and heifers are predicated upon the generalization that cows, improved to show strongly the characteristics of any of the dominant beef breeds, should weigh not less than 1050 pounds before calving in order to support consistently regular breeding, maximum lactation, and optimum weaning weights of calves. Under practical conditions the lighter weights generally reflect thinner condition rather than smaller body size. The recommendations, therefore, call for heavier feeding of the lighter cows and heifers in order to attain satisfactory condition by the end of the wintering period.

For wintering calves the expected gain and nutrient allowances presented are economical and practical where maximum gain on pasture is subsequently desired and when the animals are to be sold as feeder cattle at the end of the next grass season. When such cattle are to be fattened by full-feeding toward the end of the following grazing period, the more liberal feeding indicated under "Normal Growth" is recommended following weaning and through the winter. Protein allowances are, in light of present knowledge, considered minimum to meet the production objectives and are recommended when protein feeds are scarce and high in price. When protein is plentiful and favorably priced, increasing these allowances by 10 to 20 per cent may be desirable.

The calcium and phosphorus allowances are considered to have approximately a 25 per cent margin of safety to meet contingencies encountered in practice such as variations in availability, unfavorable calcium: phosphorus ratios, or limited vitamin D.

That the requirement for carotene or vitamin A is directly proportional to body weight rather than to energy requirements (which is proportional to a fractional power of body weight) was demonstrated by

Guilbert and Hart.[18] For optimum growth and freedom from clinical symptoms 1.5 mg. of carotene or 1000 I.U. of preformed vitamin A daily per 100 pounds body weight suffice. A level of 6.0 mg. of carotene or 3000 I.U. of vitamin A daily per 100 pounds body weight are about minimum for reproduction and for significant storage.[20] Since carotene is the normal source of vitamin A value for cattle, carotene allowances only are given in the table.

During periods of abundant intake or green pasture, vitamin A and carotene are stored in the liver and adipose tissue. So long as adequate storage remains, no carotene is required in the feed. Prolonged withdrawal while subsisting exclusively on dried, bleached forages results in depletion and deficiency. The usual manifestation in breeding herds is abortion or birth near term of dead or weak calves; in feed lots, night blindness, convulsions, and anasarca sometimes occur. With the exception of yellow corn, insignificant amounts of carotene are found in grains and mill feeds.

Requirements for Other Nutrients

Vitamins. Under usual conditions of management, beef cattle receive sufficient vitamin D from sunlight and from sun-cured roughages. The requirement for young calves according to Bechdel and co-workers[4] is about 300 I.U. per 100 pounds live weight.

As previously discussed under the section on peculiarities of ruminant nutrition, the vitamin-B complex factors apparently are synthesized in adequate amounts in the rumen provided the ration is otherwise adequate.

The need for vitamin E in the diet of cattle has not been demonstrated nor is there evidence of rumen synthesis of this vitamin. Vitamin K is synthesized by the microorganisms of the rumen.

Minerals Other than Calcium and Phosphorus. *Salt.* The daily requirement of sodium for growth is about 1.5 g. daily and for chlorine, less than 5 g. For lactating cows 11 g. of sodium and 15 g. chlorine suffice.[11, 39] Salt is used both as a nutrient and a condiment, and cattle should have free access to it. Consumption of 1.0 to 2.5 pounds a month per head is common on range and pasture—amounts greatly in excess of the minimum requirements suggested above.

Iodine. In goitrogenic areas, the use of salt containing 0.015 to 0.02 per cent potassium iodide effectively prevents thyroid enlargement and birth of dead or nonviable and hairless calves. Exact requirements have not been established. Griem and Associates[16] recommend use of salt containing 0.01 per cent potassium iodide stabilized to prevent loss of iodine.

Iron. Iron requirements of cattle are unknown; apparently the amount in ordinary feed is ample. Suspected iron deficiency reported in the past has subsequently been shown to be deficiency of copper and/or cobalt.

Copper. Copper deficiency has been reported in different parts of the world and in some cases appears to be associated with or complicated by excess molybdenum. Cattle on pastures containing 2 to 3 p.p.m.[38] and 1 to 4 p.p.m.[6] of copper in the dry matter manifested anorexia, anemia, emaciation, and diarrhea and responded to copper therapy. Pastures containing 7.5 p.p.m. were regarded as healthy. Bleaching of hair color has been associated with copper deficiency and with molybdenum toxicity which may be complicated by copper deficiency.

Cobalt. Judging from the data on composition of cobalt deficient and adequate pastures and from experiments on cobalt therapy the minimum requirement is in the order of 0.1 p.p.m. in the dry matter of the feed or about 0.1 mg. daily per 100 pounds body weight.[1, 2, 13, 34, 40]

Cobalt deficiency results in loss of appetite, progressive emaciation, and anemia. Thus far it has not been possible to demonstrate the deficiency in animals other than ruminants. Vitamin B_{12} contains cobalt, but cobalt evidently is essential to micro-biological synthesis of other entities which prevent deficiency symptoms.

Magnesium. Deficiency of magnesium causing tetany and death may result from prolonged feeding of calves on milk without grain or hay. So-called grass tetany with decreased blood serum magnesium has often been noted, but apparently it is a metabolic disturbance not primarily associated with deficiency in the forage. The requirement for calves, according to Huffman and co-workers,[24] is about 0.6 g. of magnesium daily per 100 pounds of body weight where natural feeds are the source.

Other minerals. The mineral elements listed above are those for which deficiency symptoms are known or the need for supplementation in localized parts of the world has been demonstrated. Cattle, in common with other species, require sulfur, potassium, and probably fluorine, manganese, and zinc.

In addition to molybdenum, cattle are subject to the toxic effects of excess fluorine and selenium in localized areas and sometimes from excess salts in saline drinking water. Selenium poisoning results in a dermatitis and a characteristic eroded condition of horns and hooves. Excess fluorine over a period of months results in loosening and abnormal wear of teeth and extensive abnormalities of the bony structures of the body.

PRACTICAL CONSIDERATIONS

Aside from a lack of common salt (NaCl), deficiencies common among beef cattle grazing natural vegetation, particularly on mature dried forage, are shortages of protein, energy (total digestible nutrients), phosphorus and vitamin A. Calcium deficiency is rarely encountered except in calves heavily fed on concentrates with very limited quantities of nonlegume roughage. Trace elements such as cobalt, copper, and iodine may not be supplied adequately in localized areas.

Both on farms and on ranges, the protein and total nutrients allowed or available are the most common deficiencies for efficient production. The beef animal in common with any producing unit is most efficient when working at near full capacity. Lack of sufficient energy or deficiency of protein, phosphorus, or any nutrient that reduces appetite not only affects growth rate, but also commonly leads to excessive weight losses and reproductive failure. The animal draws upon its own tissues to supplement its feed and to maintain vital functions.

Two considerations are of paramount importance from the standpoint of nutrition in relation to production: First—an adequate plane of nutrition for the breeding herd and second—the "principle of continuous growth." Regular breeding, maximum lactation, and optimum weaning weight of calves depend on keeping the breeding cows above a critical level and permitting recovery before calving of any negative nutritional balance incurred during lactation.

Continuous and rapid growth increases the proportion of nutrients recovered in body substance compared with the expenditure for maintenance. Relative development of various parts of the body is dependent not only on heredity but also on the shape of the growth curve.[19, 33] Undernutrition retards thickness growth and later maturing parts such as loin and hindquarter more than it does linear skeletal growth and early developing organs and tissues. It has been shown [19] that the use of 200 to 300 pounds of supplemental feeds given to younger cattle to promote continuous growth and efficient use of dry range forage or nutritionally deficient hay commonly will result in 100 pounds additional live weight. Such feed will replace about 500 pounds of concentrates and 400 to 500 pounds of harvested roughage required to make up this difference later in feed lots.

This over-all view of production from the calf to the final product rather than a view of isolated production phases is important. It considers not only the profit to the producer but also the maximum amount of human food that can be produced at the state or national level with the total feed available. The total tonnage of beef from available feed in the United States could be increased tremendously through use of an increased proportion for improving breeding efficiency and for promoting continuous growth during those periods of the year when feeds are nutritionally deficient or inadequate in quantity.

BIBLIOGRAPHY

Specific References

1. Askew, H. O., and Maunsell, P. W., *New Zealand J. Sci. Tech.* **19**: 337 (1937).
2. Baltzer, A. C., Killham, B. J., Duncan, C. W., and Huffman, C. F., *Mich. Agr. Expt. Sta. Quar. Bull.* **24**: 68 (1941).
3. Bartlett, S., and Cotton, A. G., *J. Dairy Res.* **9**: 263 (1938).
4. Bechdel, S. I., Hilston, N. W., and Guerrant, N. B., *J. Dairy Sci.* **20**: 432 (1937).
5. Bechdel, S. I., Honeywell, H. E., Dutcher, R. A., and Knutsen, M. H., *J. Biol. Chem.* **80**: 231 (1928).
6. Bennetts, H. W., Beck, A. B., Harley, R., and Evans, S. T., *Austral. Vet. J.* **17**: 85 (1941).
7. Cole, H. H., Huffman, C. F., Kleiber, M., Olson, T. M., and Schalk, A. F. (Fourth Report of The Committee on Animal Health of the National Research Council). *J. Animal Sci.* **4**: 183 (1945).
8. Cole, H. H., Mead, S. W., and Kleiber, M., *Calif. Agr. Expt. Sta. Bull.* **662** (1942).
9. Colin, G., *Compt. rend.* **34**: 682 (1852).
10. Dukes, H. H., "The Physiology of Domestic Animals." 721 pp. Ithaca, New York, Comstock Publishing Co. (1937).
11. DuToit, P. J., Malan, A. I., and Groenewald, J. W., *Onderstepoort J. Vet. Sci. Animal Ind.* **2**: 565 (1934).
12. Elsden, S. R., Hitchcock, M. W. S., Marshall, R. A., and Phillipson, A. T., *J. Expt. Biol.* **22**: 191 (1946).
13. Filmer, J. F., and Underwood, E. J., *Austral. Vet. J.* **13**: 57 (1937).
14. Fingerling, G., Hientzsch, G., Kunze, H., and Reifgerst, K., *Landw. Vers. Stat.* **128**: 221 (1937).
15. Goss, H., *Nutr. Abs. Revs.* **12**: 531 (1942).
16. Griem, W. B., Hart, E. B., Kalkus, J. W., and Welch, H., *Natl. Res. Council Reprint and Cir. Ser.* **111** (1942).
17 Guilbert, H. R., Gerlaugh, P., and Madsen, L. L., "Recommended Allowances for Beef Cattle." Rept. Com. on Animal Nutr., National Research Council, Washington, D. C. (1945).
18. Guilbert, H. R., and Hart, G. H., *J. Nutr.* **10**: 409 (1935).
19. Guilbert, H. R., Hart, G. H., Wagnon, K. A., and Goss, H., *Calif. Agr. Expt. Sta. Bull.* **688** (1944).
20. Guilbert, H. R., Howell, C. E., and Hart, G. H., *J. Nutr.* **19**: 91 (1940).
21. Harris, L. E., and Mitchell, H. H., *J. Nutr.* **22**: 167 (1941).
22. Hart, E. B., Bohstedt, G., Doebold, H. J., and Wegner, M. I., *J. Dairy Sci.* **22**: 785 (1939).
23. Henriques, V., and Anderson, A. C., *Hoppe-Seyler's Z. Physiol. Chem.* **92**: 21 (1914).
24. Huffman, C. F., Conley, C. L., Lightfoot, C. C., and Duncan, C. W., *J. Nutr.* **22**: 609 (1941).
25. Kellner, O., and Kohler, A., *Landw. Vers. Sta.* **53**: 1 (1900).
26. Kleiber, M., Cole, H. H., and Mead, S. W., *J. Dairy Sci.* **26**: 929 (1943).
27. Kleiber, M., Regan, W. M., and Mead, S. W., *Hilgardia* **16**: 511 (1945).
28. Krebs, K., *Biedermanns Zentralbl. B. Tierenähr.* **9**: 394 (1937).
29. Lagerlof, N., *Skand. Vet. Tidskr.* **19**: 253 (1929).
30. McElroy, L. W., and Goss, H., *J. Nutr.* **20**: 527; 541 (1940).

31. McElroy, L. W., and Goss, H., *J. Nutr.* **21**: 163; 405 (1941).
32. McElroy, L. W., and Jukes, T. H., *Proc. Soc. Expt. Biol. Med.* **45**: 296 (1940).
33. McMeekan, C. P., *J. Agr. Sci.* **30**: 276 (1940); **31**: 1 (1941).
34. McNought, K. J., *New Zealand J. Sci. Tech.* **20**: 14 (1938).
35. Müller, M., *Pflügers Arch.* **112**: 245 (1906).
36. Savage, E. S., and McCay, C. M., *J. Dairy Sci.* **25**: 595 (1942).
37. Schalk, A. F., and Amadon, R. S., *N. Dakota Agr. Expt. Sta. Bull.* **216** (1928).
38. Sjollema, B., *Biochem Z.* **267**: 151 (1933).
39. Thieler, A., Green, H. H., and DuToit, P. J., *J. Agr. Sci.* **17**: 291 (1927).
40. Underwood, E. J., and Harvey, R. J., *Austral. Vet. J.* **14**: 183 (1938).
41. Van Niel, C. B., *Physiol. Rev.* **23**: 338 (1943).
42. Wegner, M. I., Booth, A. N., Elvehjem, C. A., and Hart, E. B., *Proc. Soc. Expt. Biol. Med.* **45**: 769 (1940).
43. Wegner, M. I., Booth, A. N., Elvehjem, C. A., and Hart, E. B., *Proc. Soc. Expt Biol. Med.* **47**: 90 (1941).
44. Weiske, H., Schrodt, M., and Danger, S., *Biol.* **15**: 261 (1879).
45. Woodman, H. E., and Stewart, J., *J. Agr. Sci.* **18**: 713 (1928).
46. Zuntz, N., *Pflügers Arch.* **49**: 477 (1891).

General References

47. Armsby, H. P., "The Nutrition of Farm Animals," p. 743. New York, The Macmillan Co. (1922).
48. "Food and Life—Yearbook of Agriculture, 1939." U. S. Dept. Agr., Washington, D. C., Govt. Printing Office (1939).
49. Guilbert, H. R., and Hart, G. H., *Calif. Agr. Ext. Ser. Circ.* **131** (1946).
50. Kellner, O., "Die Ernährung der landwirtschaftlichen Nutztiere," 667 pp. Berlin, Paul Parey (1919).
51. Mangold, E., "Handbuch der Ernährung und des Stoffwechsels der landwirtschaftlichen Nutztiere," 930 pp. Berlin, Julius Springer (1932).
52. Morrison, F. B., "Feeds and Feeding," 1050 pp. Ithaca, New York, The Morrison Publ. Co. (1936).
53. National Research Council, Committee on Animal Nutrition. Recommended Nutrient Allowances for Beef Cattle, 32 pp. Washington, D. C. (1945).
54. Schneider, B. H., "Feeds of the World, Their Digestibility and Composition," 299 pp. W. Va. Agr. Expt. Sta., Morgantown, W. Va. (1947).
55. Snapp, R. R., "Beef Cattle, Their Feeding and Management in the Corn Belt States." New York, John Wiley and Sons, Inc. (1939).

Chapter XV

THE NUTRITION OF HORSES AND MULES *

P. B. Pearson

U. S. Atomic Energy Commission, Washington, D. C., and
Animal Husbandry Division, Bureau of Animal Industry, U. S. Department
of Agriculture, Beltsville, Maryland

C. F. Winchester

Animal Husbandry Division, Bureau of Animal Industry,
U. S. Department of Agriculture, Beltsville, Maryland

An appreciation of the magnitude of the horse and mule industry may be obtained from the fact that there are 11 million horses and mules in the United States[a] at the present time representing an investment of nearly a billion dollars. The cost of the animals' feed and care, alone, amounts to over a billion dollars annually. Considering the size of the industry, it appears that horses and mules deserve more scientific attention than they have received in the past.

Compared with the existing experimental data on nutrition of other species of farm animals, there is available a very small amount of information on nutrition of horses and mules. For example, there is very little information concerning differences between the various types and breeds of horses, or between horses and mules, in energy requirements for maintenance or work. As a matter of fact, data on maintenance of horses are so few that it has been necessary to use data on the energy requirements of cattle for maintenance in calculations of the feed requirements of horses. Tables of digestible nutrients, used as criteria of the values of various feeds for horses, are based largely on data obtained in digestion trials made on ruminants.

Although some information is available on protein and energy requirements of horses for maintenance and work, virtually none on requirements for pregnancy, lactation, and growth exists. It has been necessary to supplement the meager information available at the present time with estimates of nutrient requirements of pregnant and lactating mares and of growing colts based on data on maintenance, the utilization of nutrients in digestion and metabolism, and other pertinent information.

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* Some of the data included in this chapter were taken from the National Research Council Bulletin, "Recommended Nutrient Allowances for Horses," by P. B. Pearson, C. F. Winchester, and A. L. Harvey.

TABLE 98. DAILY ALLOWANCES FOR MATURE HORSES

Body Weight	Digestible Protein				Total Digestible Nutrients				Dry Matter-90% Basis				Calcium[1]	Phosphorus[1]
	Maintenance	Work			Maintenance	Work			Maintenance	Work				
		Light	Medium	Hard		Light	Medium	Hard		Light	Medium	Hard		
lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	g.	g.
400	0.31	0.38	0.46	0.52	3.9	5.1	5.9	7.3	6.2	8.2	9.4	11.0	7.3	8.5
600	0.42	0.52	0.62	0.70	5.3	6.9	8.0	9.9	8.5	11.0	12.8	14.8	9.9	11.0
800	0.53	0.65	0.77	0.87	6.6	8.6	10.0	12.3	10.6	13.8	15.9	18.4	12.2	13.7
1000	0.62	0.76	0.91	1.03	7.9	10.1	11.8	14.6	12.6	16.2	18.9	21.9	13.7	15.4
1200	0.71	0.88	1.04	1.18	9.0	11.6	13.5	16.7	14.4	18.6	21.6	25.1	15.7	17.7
1400	0.80	0.98	1.17	1.33	10.1	13.0	15.1	18.8	16.2	20.8	24.2	28.2	17.6	19.8
1600	0.88	1.09	1.29	1.47	11.1	14.4	16.7	20.7	17.8	23.0	26.7	31.0	19.4	21.8
1800	0.97	1.19	1.40	1.60	12.0	15.8	18.2	22.5	19.5	25.3	29.1	34.0	21.1	23.8
Mares – Last Quarter of Pregnancy														
400		0.46				5.4				8.6			7.8	7.8
600		0.62				7.3				11.7			10.6	10.6
800		0.77				9.0				14.4			13.1	13.1
1000		0.91				10.6				17.0			15.4	15.4
1200		1.04				12.2				19.5			17.7	17.7
1400		1.17				13.7				21.9			19.9	19.9
1600		1.30				15.2				24.3			22.1	22.1
1800		1.43				16.2				26.6			24.2	24.2
Mares – Lactating														
400		1.01				8.8				12.3			12.3	11.2
600		1.37				11.9				16.7			16.7	15.2
800		1.70				14.7				20.6			20.6	18.7
1000		2.01				17.4				24.4			24.4	22.2
1200		2.30				20.0				28.0			28.0	25.4
1400		2.59				22.4				31.4			31.4	28.5
1600		2.88				24.9				34.9			34.9	31.7
1800		3.12				27.1				37.9			37.9	34.4

[1] Calculated for horses at medium work.

The recommendations given in Tables 98 and 99 on protein and energy allowances based on limited data and on computations are necessarily tentative in nature, and serve to emphasize the present need for careful experimental work on nutrition of horses.

PHYSIOLOGICAL WORK

Efficiency. Only part of the energy expended during muscular contraction appears as useful work. The theoretical maximum efficiency of a contracting muscle is only about 40 per cent;[20] additional energy is lost in the interaction of various sets of muscles, and a considerable loss is accounted for externally in the slipping of hoofs on the ground. As a result of these energy losses, the ratio of useful work accomplished by the horse to energy expended during work is not more than 25 per cent.

The gross efficiency of the horse (useful work expressed as percentage of food energy consumed) can be calculated. For example, an 1800-pound horse averaging 8 horsepower hours of useful work a day is allowed 22.5

TABLE 99. DAILY PROTEIN AND ENERGY ALLOWANCES FOR GROWING HORSES

	600					800					1000				
	Age	Daily Gain	Dry Matter	Digestible Protein	T.D.N.	Age	Daily Gain	Dry Matter	Digestible Protein	T.D.N.	Age	Daily Gain	Dry Matter	Digestible Protein	T.D.N.
	mo.	lb.	lb.	lb.	lb.	mo.	lb.	lb.	lb.	lb.	mo.	lb.	lb.	lb.	lb.
200	3.5	1.1	6.7	0.77	4.2	2.6	1.4	7.2	0.93	4.5	2.0	1.6	7.5	1.04	4.7
400	14.0	0.6	9.1	0.57	5.7	8.0	0.9	9.9	0.80	6.2	6.0	1.2	10.2	0.94	6.4
600	42.0	0.0	10.2	0.45	6.4	19.0	0.5	11.7	0.65	7.3	14.0	0.8	12.3	0.77	7.7
800						44.0	0.0	12.6	0.54	7.9	24.0	0.5	13.8	0.74	8.6
1000											44.0	0.0	15.0	0.64	9.4

	1200					1400					1600				
200	1.9	1.9	7.7	1.06	4.8	1.2	2.5	8.2	1.22	5.1	0.9	3.3	8.5	1.28	5.3
400	5.2	1.6	10.4	1.03	6.5	4.0	2.1	11.0	1.16	6.9	3.0	2.8	11.8	1.43	7.4
600	10.0	1.2	13.3	0.93	8.3	7.5	1.6	13.4	1.13	8.4	5.5	2.4	13.9	1.33	8.7
800	17.0	0.8	14.7	0.87	9.2	12.0	1.3	15.8	1.05	9.9	9.0	1.8	16.6	1.23	10.4
1000	25.0	0.4	16.2	0.85	10.1	19.5	0.8	17.0	0.97	10.6	13.0	1.2	18.4	1.17	11.5
1200	45.0	0.0	17.1	0.72	10.7	26.0	0.4	18.4	0.95	11.5	19.0	1.0	19.5	1.11	12.2
1400						45.0	0.0	19.4	0.81	12.1	26.0	0.5	20.6	1.06	12.9
1600											48.0	0.0	21.1	0.86	13.2

	1800				
200	0.6	4.0	9.0	1.39	5.6
400	2.4	3.8	12.3	1.50	7.7
600	4.5	3.3	14.4	1.49	9.0
800	7.0	2.7	17.0	1.44	10.6
1000	9.6	2.1	19.5	1.40	12.2
1200	13.2	1.6	20.8	1.34	13.0
1400	18.4	1.0	22.1	1.26	13.8
1600	26.4	0.5	22.7	1.18	14.2
1800	48.0	0.0	23.2	0.95	14.5

pounds T.D.N. (total digestible nutrients) per day. Useful work and food energy can be expressed in a common unit using the conversion factors 641.3 Calories to equal 1 horsepower-hour, and 1814 Calories to equal 1 pound of T.D.N.[3] The gross efficiency equals $\frac{8 \times 641.3}{22.5 \times 1814} \times 100$ or 12.6 per cent. The efficiency levels of horses of all sizes, as calculated from data given in Table 98, are equal because the nutrient allowances as well as the work levels postulated in the table vary with the same power of body weight.

Gross efficiency declines as the work day is shortened; and, since most farm horses average less than 8 hours of useful work daily, most of them work at efficiency levels below 12.6 per cent. Nevertheless, this level of efficiency can be attained with good management, and it equals the drawbar efficiency of most farm tractors in use at the present time. Moreover, the lifetime efficiency of the horse compares very favorably with that of a machine when it is realized that an enormous amount of human labor is consumed in production, maintenance, and repair of tractors, whereas relatively little labor is required for production and maintenance of horses.

Furthermore, to a large extent horses utilize energy in the raw or unprocessed form, while fuels for machines must be highly refined by expensive processes and usually transported long distances.

Since a draft horse is not expected to exert a continuous pull throughout an ordinary work day much greater than a tenth of its body weight, only a large horse (1500 pounds or larger) ordinarily is worked at the rate of 1 horsepower during the entire day. On the other hand, horses working at maximum load for short periods can overcome draft resistance of 7 to 13 horsepower, and the animal's total energy production during these periods of maximum load is about 100 times as great as the basal metabolic rate. This is a tremendous expenditure of energy compared to that of ordinary "hard" work during which about eight times the energy of basal metabolism is expended.[3]

PROTEIN REQUIREMENTS

Maintenance and Work. The protein allowances for maintenance given in Table 98 are about four times the protein of endogenous metabolism.[3] The following experimental evidence demonstrates that the allowances given in Table 98 are at least adequate. Harvey et al.[19] have shown that a daily ration in which the protein was supplied entirely by 3 pounds of oats and 20 pounds of timothy hay (equivalent to 0.86 pound of digestible protein [36]) was sufficient to keep 1680-pound Percherons in positive nitrogen balance. The protein supplied was sufficient, not only during rest, but also during work at rates as high as 1.27 horsepower for over four hours daily. The level of protein supplied in these experiments was almost identical with the allowance given in Table 98 for maintenance. Nitsche [41] reports that the digestible crude protein requirement of resting horses is from 53 to 68 g. per 100 kg. of body weight, the equivalent of 0.53 to 0.68 pound for a 1000-pound horse. The allowance of 0.6 pound of digestible protein for a 1000-pound horse for maintenance compares favorably with these experimental results.

Harvey's results, demonstrating that the maintenance level of protein is sufficient for working horses, are supported by a respectable body of experimental data.[13] Nevertheless, the protein allowances given in Table 98 for working horses are greater than this evidence indicates is necessary. The reason is that the feeds which research and experience have shown to be best suited for horses contain sufficient protein when the energy requirements are met, to provide the allowances given in Table 98.

The allowances for animals of various sizes are based on the assumption that the protein, energy, and dry matter requirements for maintenance, growth, work, and milk production vary with the the three-fourths power of body weight.[8, 27]

It should be noted that, according to Mitchell,[35] the net protein requirement for maintenance is 12.5 mg. of protein per Calorie of basal heat production in young and mature animals of various species. Calculated on this basis, the minimum requirements of young animals are somewhat higher than the recommendations made in Table 99.

Mares, During Pregnancy. It has been necessary to estimate the protein requirements of pregnant mares since reliable experimental data on these requirements do not appear in the literature. Using Morrison's[36] figures for birth weights of foals, and assuming that the figures cited by Brody[5] on weight and protein of the placenta and amniotic fluid of cattle are similar to those of the horse, the following figures have been obtained for an 1800-pound draft mare:

	Weight	*Protein*	
	lb.	*%*	*lb.*
Foal at birth	120	14.2	17.0
Amniotic fluid	49	3.4	1.7
Placenta	24	12.2	2.9
		Total	21.6

Since at least half the fetal protein, or 10.8 pounds, is assimilated during the last quarter of pregnancy, the mean daily increment is 0.13 pound (i.e., $\frac{10.8}{85}$ days equals 0.13 pound protein gained daily). An allowance of one-tenth of the maintenance protein requirement of the mare has been estimated to be sufficient to meet the needs for metabolic activity of the fetus. This is equal to about 0.10 pound digestible protein daily for a fetus carried by an 1800-pound mare. Assuming the biological value of the feed protein to be 50 per cent, the ration must be increased over maintenance by $2(0.13 + 0.10)$ or 0.46 pound of digestible protein daily for a 1800-pound mare during the last quarter of pregnancy for incorporation in the fetus, integuments, and amniotic fluid, and metabolic activity of the fetus. The total daily protein requirement of an 1800-pound draft mare during the last quarter of pregnancy is equal to her maintenance requirement of 0.97 pound plus 0.46 pound for the fetus, or 1.43 pounds of digestible protein daily.

Ordinarily, mares are fed only a maintenance ration during all but the last part of pregnancy. This practice seems reasonable in view of the fact that the daily increase in fetal weight is extremely small during the first three-quarters of the period of pregnancy.

Mares, During Lactation. The protein requirements of lactating mares have not been determined experimentally and must be obtained by calculation. The daily milk yield of draft mares has been reported to be from 26 to 77 pounds, while an average of its composition has been found to be 2 per cent protein, 10.1 per cent T.D.N., and 1.1 per cent fat.[36] Assuming an average daily milk production of 50 pounds,* the daily secretion of protein in the milk is 1 pound; and if the biological value of ingested protein is assumed to be 50 per cent, a 1600-pound mare must be allowed 2 pounds of digestible protein daily above her 0.88-pound maintenance requirement, or 2.88 pounds of digestible protein daily.

Colts After Weaning. Experimental data on the nutritional requirements of growing horses are not sufficient to form a basis for recommendations, and therefore it has been necessary to approximate these requirements by means of calculations based on data on growth rates, chemical composition of horses, and maintenance requirement. Before the computations could be made it was necessary to make the following assumptions: (1) the biological value of digestible protein in the feed is 50 per cent; (2) the protein content of the foal at birth is the same as that of the calf, namely 14.2 per cent;[3] (3) the relationship between age of the colt and its chemical composition is similar to that of the calf;[37] and (4) maintenance requirements are four times the level of the protein equivalent of endogenous nitrogen metabolism.[3] On the basis of these assumptions, the protein requirements of growing colts can be calculated as shown below.

DAILY PROTEIN REQUIREMENTS OF WEANED COLTS

Body Wt. lb.	Age Mo.	Daily Gain		Protein Required in Ration for Growth lb.	Protein Required for Maintenance lb.	Total Protein Required lb.
		Total lb.	Protein lb.			
400	2.4	3.8	0.57	1.15	0.36	1.5
1000	9.6	2.1	0.35	0.70	0.70	1.4

Protein allowances for growing horses of various mature sizes are given in Table 99.

ENERGY REQUIREMENTS

Maintenance. According to Morrison,[36] mature, idle horses have been maintained for considerable periods in careful experiments on 6.4 to 7.0 pounds T.D.N. (total digestible nutrients) daily per 1000 pounds live weight. This compares favorably with the figure 6.75 pounds T.D.N. per day which Brody[3] postulates as the cost of maintenance of a 1000-pound animal on the assumption that maintenance is twice the basal metabolic rate. The energy allowance for maintenance, Table 98, is twice the basal metabolic rate, plus a safety factor of one-third basal metabolism.

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* Estimates of milk produced by mares based on growth rates of foals indicate that the milk production of mares is very near this assumed level.

Work. The energy allowances given for horses at light work are three times basal metabolism. This corresponds closely to Brody's allowances for horses working 2 to 3 hours a day, and to Morrison's standard for horses at light work.

Energy allowances for horses at medium work are 3½ times basal metabolism. These are comparable to Brody's allowances for horses working 4 to 5 hours a day, and to Morrison's standard for horses at medium work. Except during periods of peak load, the actual daily work-period of farm horses is seldom more than 5 hours a day and therefore the energy allowances for horses at medium work are sufficient for all but those horses that are at very heavy work. The nature of their labor compels horses to stand in place during a large fraction of the work day and this standing time cannot be considered work. Actually, horses are able to rest every bit as well while standing as they do while lying down.[4, 57]

Horses at hard work are allowed 4⅓ times the energy of basal metabolism, or maintenance plus twice the energy level of basal metabolism; this is sufficient energy for 8 hours of work per day.

Pregnant Mares. During the first three-quarters of the pregnancy period, when growth rate of the fetus is relatively low, the maintenance ration is adequate for the mare and the fetus as well.[3] The energy requirements of the mare during the last quarter of pregnancy must be obtained by computation since data on these requirements do not appear in the literature. An allowance must be made for an increase in the metabolic rate that is of the order of 30 per cent during the last quarter of pregnancy in cows, and by analogy and on the basis of scanty data, in mares as well.[3]

The net nutrients incorporated in the fetus, placenta, and amniotic fluid during the last quarter of pregnancy are calculated for an 1800-pound draft mare as follows:

	Wt. *lb.*	Protein		Fat			T.D.N. Energy *lb.*
		%	*lb.*	*%*	*lb.*	*lb.* × *2.25*	
Foal at birth	120	14.2	17.0	2.5	3.0	6.8	23.8
Amniotic fluid	49	3.4	1.7	0.9	0.45	1.0	2.7
Placenta	24	12.2	2.9	0.9	0.2	0.5	3.4
Total							29.9

The mean energy in T.D.N. gained daily by the fetus, integuments, and amniotic fluid can be obtained by dividing the result obtained above by the number of days in the last quarter of pregnancy, or: $\frac{29.9}{85} = 0.35$ pound of T.D.N. Assuming the availability of nutrients for growth of the fetus to be 60 per cent, $\frac{0.35}{0.6}$ or 0.6 pound T.D.N. must be allowed daily. The energy requirement of an 1800-pound draft mare during the last quarter of pregnancy is:

	T.D.N. Daily *lb.*
For fetus, placenta, and amniotic fluid	0.6
Normal maintenance	12.0
Heat increment of pregnancy (30% maintenance)	3.6
Total	16.2

Mares, During Lactation. Assuming that the mean daily milk production of 1600-pound mares is 50 pounds, and that the T.D.N. content of mares' milk is 10.1 per cent,[36] the T.D.N. daily secreted as milk is about 5 pounds. If the availability of feed nutrients for milk production is assumed to be 60 per cent, the daily allowance of digestible nutrients for milk should be 8.33 pounds T.D.N.

In addition to the allowances for maintenance and for nutrients to be incorporated in the milk, an allowance must be made for the heat increment of lactation. Statements in the literature to the effect that lactation does not increase heat production are based on measurements of metabolism during fast, according to Brody,[3] who states further that: "Under ordinary conditions, of course, lactating animals do not fast; indeed, they consume two or three times as much food as non-lactating animals,—their heat production is perhaps twice as great as that of non-lactating animals, the exact value depending on the lactation level, and therefore food intake." The heat increment of lactation may be assumed to be 50 per cent of maintenance at the lactation level used in the calculations. The daily energy requirements of a 1600-pound draft mare in lactation may be estimated as follows:

	T.D.N. Daily *lb.*
Maintenance	11.1
Heat increment	5.5
For T.D.N. in milk	8.3
Total	24.9

When comparison is made on the bases of size of animal and energy secreted as milk, this allowance is about equal to the standard allowance for a dairy cow.

Colts After Weaning. Experimental data on the nutrient requirements of growing horses are very meager, and estimates of the energy requirements of colts must, therefore, be based on the information available on growth rates, metabolism, activity, and chemical changes of the body composition of the horse with age.

Sources of data on growth rates of horses of various mature sizes are as follows: 1800-pound Percherons;[34] 1400-pound Percherons and horses of around 800-pound body weight;[3] 1100-pound horses;[36] and 400-pound ponies.[11]

In calculating the energy requirements of growing colts, the following assumptions were made: (1) the biological value of protein in the ration is 50 per cent; (2) net availability of digestible nutrients is 70 per cent for maintenance and 60 per cent for growth; (3) one pound T.D.N. equals 1814 Calories of energy;[3] (4) the protein and fat content of the newly born foal are the same as those of the calf, namely 14.2 and 2.5 per cent respectively;[3] (5) the relationship between age of the colt and chemical composition of its body is similar to that of the calf;[37] (6) the energy cost of activity is one-fifth maintenance in the young colt, and declines with age.

The following example shows how the energy requirements of a 400-pound draft colt 2.7 months of age, making a daily gain of 3.8 pounds, were estimated.

		Daily Requirements			*T.D.N. lb.*
For Maintenance:					
400 (Body weight in lb.)	×	15.42 (Maintenance requirement in Calories[3])	=	6168 Calories (24-hour, net maintenance)	
6168	÷	1814 (Calories per lb. T.D.N.[3])	=	3.4 lb. T.D.N.	
3.4	÷	0.7 (Net availability for maintenance)	=		4.9
For Activity (one-fifth maintenance)			=		1.0
For Protein:					
3.8 (Daily gain in lb.)	×	0.149 (Protein in body)	=	0.57 lb. protein net requirement	
0.57	÷	0.5 (Biological value of protein)	=		1.14

For Fat:

3.8 (Daily gain in lb.)	×	0.45 (Fat in body)	= 0.18 lb. fat, net gain	
0.18	×	2.25 (Lb. T.D.N. per lb. fat)	= 0.40 lb. T.D.N., net gain of body fat	
0.40	÷	0.6 (Net availability for growth)	=	0.67
		Total daily energy requirements		7.71

Additional allowances must be given growing horses at work. These allowances can be estimated from Table 98, allowances for mature horses for maintenance and work. For example, if a mature 1200-pound horse is allowed 9 pounds T.D.N. for maintenance and 11.6 pounds T.D.N. while at light work, a growing 1200-pound horse that will weigh 1600 pounds when fully grown, at light work, must be allowed 11.6 − 9, or 2.6 pounds T.D.N., in addition to the regular allowance of 12.2 pounds T.D.N., or a total 14.8 pounds T.D.N. per day.

MINERALS

Calcium, phosphorus, iodine, and sodium chloride are known to be essential for normal growth and physiological functions of the horse and mule. Since magnesium is a normal constituent of bone, it would be expected that this is also a dietary essential for Equidae. On the basis of work with other species it would be expected that other mineral elements are essential and, until we have evidence to the contrary, it is a safe practice to consider them among the nutrients to be provided for horses and mules.

The proper development of the skeletal structures is probably more important in the horse and mule than in other species of domestic animals. The strain and stress on the skeletal structures of animals required to develop maximum energy outputs such as the race horse running at its greatest speed or the draft horse under heavy loads makes the mineral nutrition of the horse of paramount importance. The thoroughbred, trained and put on the race track at the early age of 2 years, probably has a higher requirement for many nutrients and especially for calcium and phosphorus than horses allowed to become more mature before being trained for work.

Very little is known about the relationship of nutrition to the etiology of various exostoses commonly seen in the horse such as spavins, ringbones, and other bone diseases. Following the outbreak of equine osteomalacia in central Illinois,[30] the incidence of spavins, ringbones, and other bone diseases was believed to be increased. Kintner and Holt [26] reported that the admission rates of horses to army veterinary hospitals were much higher when the animals were fed a ration low in calcium than when the ration was supplemented with calcium. The incidence of various types of exostoses was higher among the horses on a calcium-deficient ration than on rations adequate with respect to this element.

Calcium and Phosphorus. A condition in horses manifested by rarefaction or softening of the bone has been encountered in various parts of the world. The condition has been referred to in the literature by various names such as osteomalacia, osteoporosis, osteodystrophia fibrosa, and other terms. It appears that the condition may be brought about by a deficiency of either calcium or phosphorus or by imbalance in the diet of these two elements. The widespread occurrence of the malady among army horses and mules in South Africa was described in 1906 by Lane.[29] The etiology of the disease was not known at that time and by some it was thought to be of pathogenic origin. However, Lane was able to correct the condition by feeding a good ration.

The characteristic symptoms of osteodystrophia fibrosa or osteomalacia have been described by Kintner and Holt[26] as follows: "The disease develops gradually with an intermittent shifting lameness with no obvious cause, usually manifested by a characteristic shortening of the stride of either the front or hind legs or both. This lameness is increased by weight bearing; it may disappear on rest only to recur in some other joint. While standing the animal usually shifts its weight, thus resting affected parts. The shoulder and hip joints are involved commonly. As the disease progresses, the lameness becomes more marked and the stride exceedingly shortened. Some cases exhibit proliferative changes of the facial bones." Longitudinal striations indicating a decalcification process frequently occur in the compact portion of the metacarpal bone. Serum calcium levels are frequently low while there is an increase in the inorganic phosphorus.

Osteodystrophia fibrosa was studied experimentally by Nurni[42] and by Nurni and Aoki[43] in Japan and by Sturges and Crawford[53] in India. These workers produced the disease by feeding rations low in calcium and high in phosphorus. The disease occurred in the Philippine Islands on a ration providing 12.9 g. of calcium and 22.0 g. of phosphorus daily, according to Kintner and Holt.[26] These workers emphasized the ratio of calcium to phosphorus as an important factor in the production of the disease. It is of some significance that the incidence of the disease in the Philippine Islands was found to be about three times higher in horses than in mules on similar dietary regimens.

While some data are available on the requirements of the horse for calcium and phosphorus there are wide variations in the figures. The requirements are undoubtedly higher for the young growing animal than for the mature animal. Studies on the inorganic phosphorus content of the blood of growing horses[44] show that the level at birth is around 5.3

mg. per 100 ml. of serum and that, by the time maturity is reached, the level has declined to about 3.4 mg. per 100 ml. of serum. On the basis of these data and calculated retentions, it is apparent that young growing animals require a higher proportion of calcium and phosphorus in their diet than do mature animals.

The requirements of the growing colt have been estimated by Harvey et al.[17] at 25 g. each per day for calcium and phosphorus. This is considerably higher than the levels proposed by Mitchell,[33] who estimates that a 400-pound colt requires about 19 g. of calcium and 13 g. of phosphorus. This would be equivalent to about 0.42 per cent of calcium and 0.29 per cent of phosphorus in the ration on a dry basis. The requirements on a percentage basis decrease as the animal matures.

TABLE 100. CALCIUM AND PHOSPHORUS ALLOWANCES FOR GROWING HORSES

Weight lb.	600 g.	800 g.	1000 g.	1200 g.	1400 g.	1600 g.	1800 g.
200	7.9	9.8	12.3	14.3	17.9	20.8	24.5
400	8.7	10.8	13.4	16.1	20.5	24.6	27.9
600	7.8	10.6	13.4	16.9	21.3	24.6	27.4
800		9.7	12.8	15.3	20.1	24.9	27.0
1000			11.6	14.7	17.8	22.6	26.5
1200				12.4	15.9	19.5	23.6
1400					14.1	16.8	21.1
1600						15.3	18.3
1800							16.8
Phosphorus Per Day							
200	7.3	8.8	10.6	12.2	14.9	17.7	20.4
400	9.1	10.8	12.5	14.6	17.5	21.4	22.3
600	9.3	11.2	13.4	16.3	18.9	22.1	22.9
800		10.9	13.0	15.3	18.7	23.3	23.9
1000			12.9	15.4	17.8	22.6	23.9
1200				14.0	16.7	20.4	22.6
1400					15.8	19.6	22.0
1600						17.2	20.6
1800							18.9

The calcium and phosphorus allowances for horses of various mature weights are shown in Table 100.

Information on the effect of work on the requirements for minerals is very meager. Harvey and associates[18] measured the effect of hard work on the retention of calcium and phosphorus. They reported that various amounts of work did not seem to affect significantly either the calcium or phosphorus balances of horses.

Salt. Sodium, potassium, and chlorine are all known to be essential for the normal physiological performance of the animal. Potassium is normally present in plants in amounts sufficient to meet the needs of herbivorous animals. The amounts of sodium and chlorine present in feeds of plant origin tend to be rather low. The common salts of sodium and potassium are freely soluble and readily absorbed from the intestine.

The excretion of sodium chloride by the renal pathway follows very closely the amount ingested. No provision is made for storing appreciable amounts of sodium chloride. When the intake is low the excretion is reduced to a very low level in an apparent effort to conserve the meager supply for vital functions. Large amounts of sodium chloride may be lost from the body through perspiration especially by horses at hard work during hot weather. The amount of sodium chloride that may be lost through perspiration by horses and mules is unknown, but on the basis of data on human beings, it must be considerable.

A deficiency of sodium chloride in human beings is accompanied by anorexia and nausea. Miners after profuse sweating frequently develop cramps if they drink large amounts of water without added salt to replace that lost from the body. Horses subjected to heavy work, especially during hot weather, should be provided with adequate salt and should be allowed to drink what water they desire at intervals of about 1 hour. Where they have been worked hard for 3 or 4 hours they should not be allowed to drink all the water they want while they are still hot and sweating. An acute salt deficiency that may be brought on by a low intake and copious sweating is accompanied by fatigue and exhaustion.[32] A deficiency of salt over a longer period of time results in lowered efficiency in utilization of proteins.[32, 55]

The quantitative requirements of the horse for salt have not been accurately established, and it is probable that they may consume more than enough to meet their needs if they have free access to it. Since the requirements vary so widely depending on the amount of work performed and the temperature, the best plan is to supply salt *ad libitum* to horses so that they can consume what they want. It may be provided either as flake salt or in block form. Horses having free access to flake salt consumed about 50 g. daily per head,[22] whereas mules used for heavy farm work consumed only about 11 g. per 1000 pounds of body weight when they were fed block salt.[54]

Iodine. A small amount of iodine is essential for reproduction and normal physiological processes. In widely distributed areas of the world and especially in high mountainous regions, soils, plants, and water are very low in iodine. The iodine deficient areas of the United States include sections of the states of Wisconsin, Ohio, Iowa, Indiana, Illinois, Michigan, Montana, Nebraska, New York, the Dakotas, Utah, Nevada, Colorado, Oregon, California, and Washington. (See Figure 28, Chapter XIII.)

Iodine exerts its physiological effects through the thyroid gland as the hormone thyroxine. Visible evidence of iodine deficiency occurs most frequently in newborn foals (see Figure 30) which are frequently born dead, or if alive, are weak and unable to stand to nurse. The breathing may be labored and the pulse rate high.

The most effective means of supplying iodine to horses in proper amounts is through the salt. The iodine requirements of various species have been reviewed by Griem et al.[14] On the basis of the recommendation of the Study Committee on Endemic Goiter of the American Public Health Association, iodized salt is now formulated with one part of potassium iodide in 10,000 parts of salt. This is 0.01 per cent of potassium iodide, or 0.0076 per cent iodine. The feeding of salt iodized at this level would normally furnish several times the iodine requirement for pregnant mares.

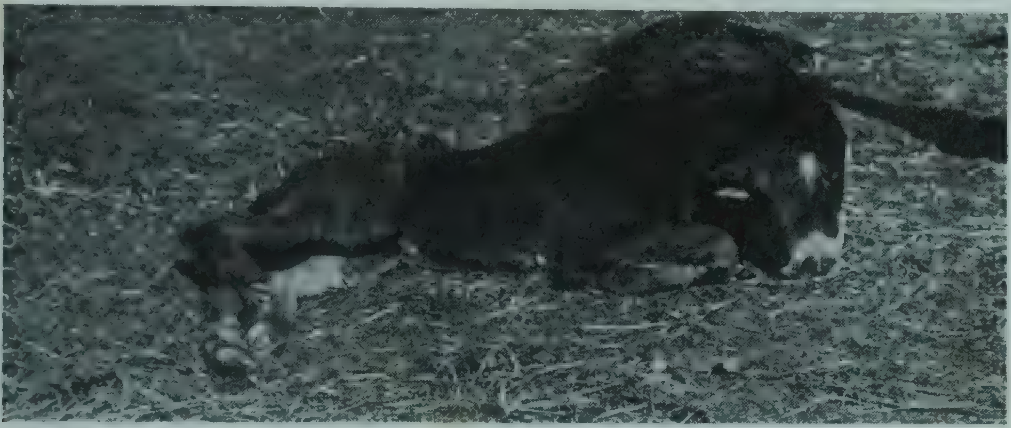


FIG. 30. Newborn weak colt affected with simple goiter due to deficiency of iodine during prenatal period. (Courtesy of the Western Wash. Agr. Expt. Sta.)

Other Essential Minerals. Other elements, particularly cobalt and copper, are known to be dietary essentials for cattle and sheep. There are well defined areas in various parts of the world where the quantities of these elements in the natural feeds are insufficient to permit successful production of cattle and sheep without supplementation of one or both of these elements.

There are no authentic reports of horses suffering from a deficiency of cobalt even in areas where the condition is endemic. Filmer[12] reports that in western Australia horses are not susceptible to enzootic marasmus. It appears that cobalt either is not a dietary essential for the horse or that their requirements are much lower than those of cattle or sheep.

Bennetts and Beck[2] in their discussion of enzootic ataxia, a disease occurring in lambs in western Australia due to a deficiency of copper, suggest that foals in this area may show abnormal manifestations. The clinical features observed in foals are malnutrition and abnormalities in structure and posture of the limbs.

Selenium Toxicity. A condition known as "alkali disease" has been a problem of considerable importance for many years in sections of the

Great Plains area of the United States and in various other parts of the world. The malady was first reported among horses in 1856 by Madison,[31] an army surgeon stationed at Fort Randall, in what was then the Territory of Nebraska. There is reason to believe that Marco Polo encountered the disease in his travels on the frontier of China.[38] More recently the disease has been studied by Moxon.[38]

The condition now known to be due to selenium poisoning has been referred to in horses as blind staggers, alkali disease, and by other local terms. The characteristic symptoms of selenium toxicity in horses are loss of the long hair from the tail and mane. Frequently a ring appears on the wall of the hoof below the coronary band, and in more advanced cases the hoof gradually separates from the foot and may be sloughed off. This is shown in Figure 31. Colts are sometimes born with deformed hoofs. In the terminal stage, blindness and varying degrees of paralysis may occur. Chronic selenium toxicity occurs when animals consume feed containing from 5 to 40 micrograms of selenium per gram on a dry basis. While recent work suggests that the toxicity of selenium may be counteracted by feeding small amounts of arsenic,[10, 39] this is still in the experimental stage so far as horses are concerned.

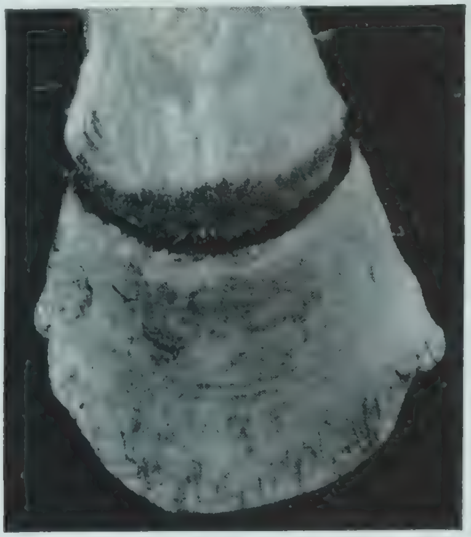


FIG. 31. The separation of the hoof from the foot of a horse that died after it had been on seleniferous feeds for only eight weeks. (Courtesy of the South Dakota Agr. Expt. Sta.)

Other Toxic Elements. There have been reports of maladies in horses that have been attributed to an excess of other mineral elements. Fluorine may occur in untreated rock phosphates in amounts sufficient to be toxic to other species. While no experimental information is available on the toxicity of fluorine for the horse the feeding of rock phosphate should be avoided.

It has recently been suggested[7] that an excess of manganese may be the cause of a condition known as "forage anemia" which occurs in natural forest pastures of Scandinavia and Finland. Affected animals show signs of anemia, decreased blood volume, and low red cell count. Oedema and emaciation occur in spite of good appetite. The pastures in these areas are frequently very high in manganese. However, feeding experiments have not substantiated the theory that forage anemia is due to an excess of manganese.

VITAMINS

Information on the quantitative vitamin requirements of the horse is very meager, and the question as to whether or not certain vitamins are required at all by Equidae has yet to be answered. The horse is a monogastric herbivorous animal and it would not, therefore, be surprising if it differs from ruminants in respect to its requirements for some of the B-vitamins. On the basis of present information it would appear that the nutrition and feeding of horses with respect to vitamins is less of a problem than it is with some other domestic animals. However, this impression may be due to the limited amount of information available on the nutritional requirements of the horse.

Carotene. Carotene is the precursor of vitamin A (see Chapter XXI in Volume I) and is the form in which this factor occurs in natural feeds consumed by horses. Horses on good quality pasture may consume many times the amount of carotene necessary for their daily requirements. The animal has the ability to convert carotene to vitamin A and to store relatively large amounts of it in the liver. Vitamin A *per se* is supplied in cod liver oil or other fish oils.

The amount of carotene present in forage is indicated by the degree of green color. Forage allowed to reach the seed stage or exposed to rains during the drying process is likely to have lost a high proportion of its vitamin A value. The intake of carotene by horses fed rations devoid of good quality green hay or silage is likely to be below their requirements. No ill effects may be apparent for several months or a year provided the animals have a good store of vitamin A. Nevertheless, it is sound nutritional practice to provide horses with some feeds that will supply at least the minimum requirements, and higher amounts should be provided for mares in foal.

The effects of a vitamin A deficiency in horses have been studied by Howell, Hart and Ittner,[21] Schmidt,[51] and Klemola.[28] The deficiency is characterized by night blindness, lachrymation, keratinization of the cornea, respiratory symptoms, abscesses of the sublingual gland, incoordination, reproductive difficulties, capricious appetite, and progressive weakness. The hoofs of deficient animals may show a pathological exuberance similar to increased scaling of epidermis. That the leg bones may be affected is indicated by failure of mineralization of the Haversian systems of these bones (Figure 32). A deficiency of vitamin A does not appear to be the cause of the joint lesions that are sometimes encountered in horses.[5, 16]

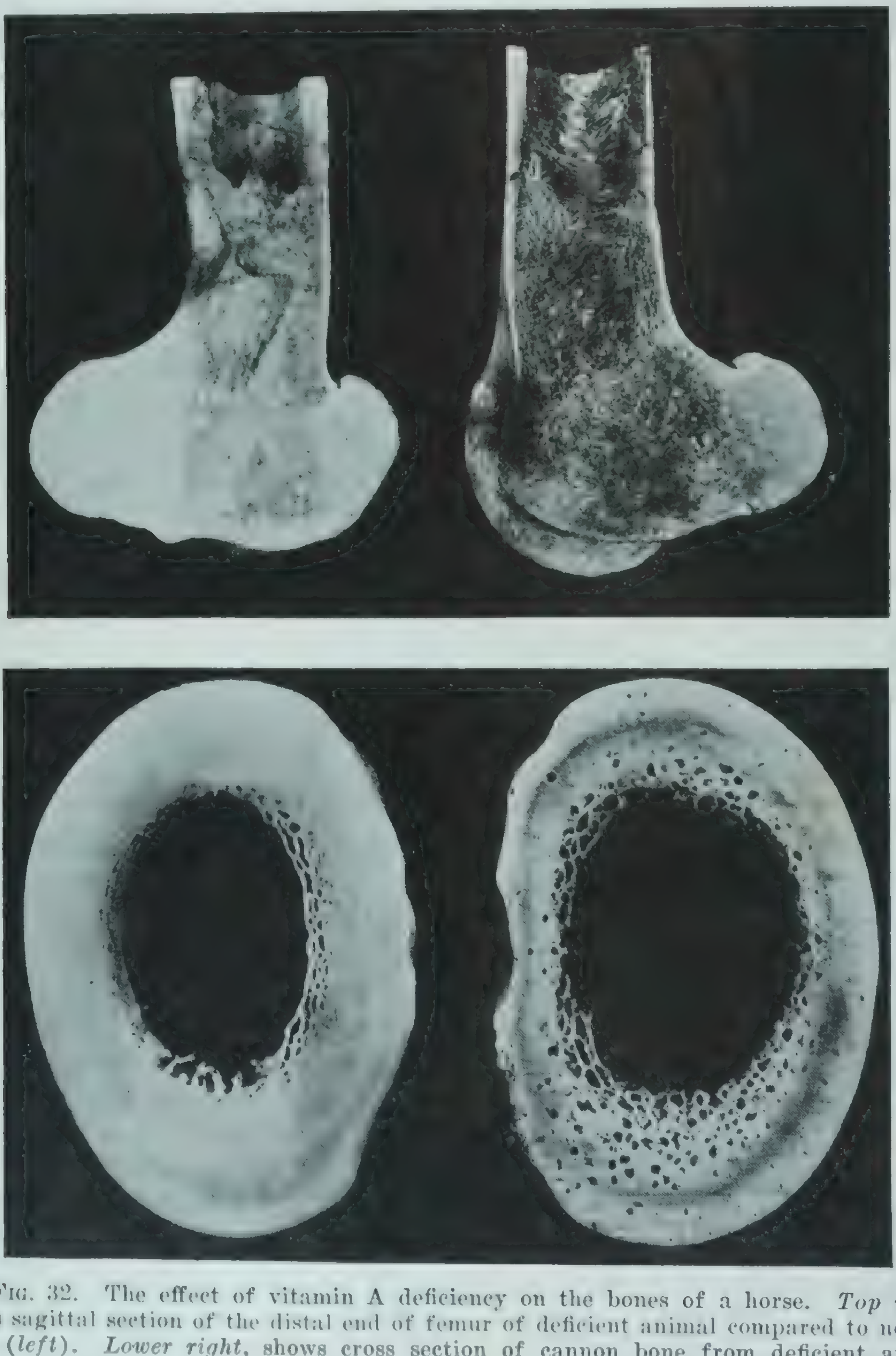


FIG. 32. The effect of vitamin A deficiency on the bones of a horse. *Top right*, shows sagittal section of the distal end of femur of deficient animal compared to normal bone (*left*). *Lower right*, shows cross section of cannon bone from deficient animal compared with normal bone on left. (Courtesy of the Calif. Agr. Expt. Sta.)

The quantitative requirements of the horse for vitamin A have been studied by Guilbert, Howell and Hart.[15] Allowances are in terms of carotene, the precursor of vitamin A, and the form available in the feeds ordinarily consumed by horses. Levels of 1.4 to 1.5 mg. of carotene per 100 pounds of body weight are reported to meet the minimum daily requirements of the horse.[15] This level probably does not allow for adequate storage nor does it meet the demands for reproduction and other special functions. For this reason the allowances recommended for both growing and mature horses are on the basis of 5.0 mg. per 100 pounds of body weight per day. This should be sufficient to build up and maintain body reserves and to meet the various physiological functions such as reproduction and lactation.

Vitamin D. Under normal farm conditions, where horses are worked regularly and are exposed to sunshine, they probably do not need added amounts of vitamin D. Where they are confined or where exposure to sunshine is restricted, or if they are fed for rapid growth and strenuous work such as racing at an early age, there may be some basis for supplying extra amounts of vitamin D. Experimental data on the requirements of the horse for vitamin D are not available. On the basis of information on other species 300 I.U. of vitamin D per 100 pounds of live weight daily should be adequate to meet the needs of horses.

B-Vitamins. Evidence that some of the B-vitamins may be dietary essentials for the horse was first presented by Naito et al.[40] Carlstrom and Hjarre [6] reported that horses fed rations deficient in the B-vitamins became emaciated, developed anorexia, and incoordination of movements. Evidence supporting the earlier observations that horses require at least some of the B-vitamins has been reported by Pearson et al.[49] It has been estimated on the basis of growth and excretion studies with Shetland ponies that 2.0 mg. of riboflavin per 100 pounds of body weight daily meets the requirements of the horse for this vitamin.[49, 50]

Jones [24] has presented evidence suggesting that iridocyclitis or periodic ophthalmia may be due to a deficiency of riboflavin. The symptoms encountered are lachrymation, exudate of the anterior chamber, and ptosis. In advanced stages cataracts, vitreous opacities, and retinal detachment may occur. More recently it has been reported [25] that the administration of large doses of riboflavin is ineffective in curing periodic ophthalmia, but there is evidence that low riboflavin diets result in a higher incidence of the disease. Further work is needed before any conclusions can be drawn on the exact relationship of riboflavin to periodic ophthalmia.

Evidence has been presented indicating that nicotinic acid is synthesized by the horse.[23, 46] It was found that horses made normal gains on rations that provided approximately 0.10 mg. of nicotinic acid per kilogram of body weight per day. When the daily intake was reduced to 0.01 mg. per kilogram of body weight the amount excreted in the urine and feces each exceeded the intake. This could be accounted for only on the basis of synthesis since the animals were gaining weight. It is of interest from a comparative biochemical standpoint that the chief end product of nicotinic acid metabolism in the horse is not N'methylnicotinamide as in the dog, man, or rat. Recently it has been shown that the horse can convert dietary tryptophan to nicotinic acid.[52] It would, therefore, be expected that the need of the horse for a dietary source of nicotinic acid may be influenced by the amount of tryptophan in the diet.

Urinary excretion studies with horses definitely show that the amount of pantothenic acid excreted by the renal pathway varies with the amount ingested.[47] Shetland ponies on a daily intake of approximately 40 micrograms per kilogram of body weight appeared to be equally as healthy as animals receiving higher levels. Whether or not pantothenic acid is a dietary essential for the horse is not certain at present, but it does appear that on rations made up of natural feeds, normally consumed by horses, there is little danger of a deficiency of pantothenic acid.

The amounts of some of the B-vitamins in the colostrum and milk of mares have been studied by Pearson.[45] The information is of interest from a comparative standpoint and may find application in feeding orphaned foals. The colostrum was found to contain an average of 38 micrograms of thiamine, 138 micrograms of riboflavin, 160 micrograms of nicotinic acid, and 747 micrograms of pantothenic acid per 100 ml. The corresponding values for the milk were 16, 40, 50, and 331 micrograms per 100 ml. for the respective vitamins. The colostrum is richer in all of the four vitamins than is milk. It is of interest that cow's milk is richer in each of the four vitamins than mare's milk.

Other Vitamins. The need for a dietary source of tocopherol or vitamin E in the rations of horses has not been demonstrated experimentally, and there is little evidence to substantiate the use of vitamin E in the treatment of sterility in horses. Vogt-Moller[56] reported negative results from vitamin E therapy in the treatment of mares suffering from early or late abortion. Furthermore, vitamin E is widely distributed in the feeds normally consumed by horses.

There is no evidence to indicate that ascorbic acid is a dietary essential for the horse. Following the ingestion of synthetic ascorbic acid by the horse, less than 2 per cent was found to be excreted in the urine,[48] and since much larger amounts than this are recovered when it is administered intravenously, the evidence suggests considerable destruction of this vitamin in the digestive tract. Following an investigation by Davis and Cole[8] on ascorbic acid therapy in the treatment of mares with irregular breeding records, these workers concluded that additional data were necessary before any conclusions could be drawn.

It is of interest to note that the ascorbic acid content of mare's milk is about five times that of cow's milk. The reduced ascorbic acid content of mare's milk is around 12 mg. per 100 ml.[45]

Other Nutritional Disturbances. A condition commonly referred to in horses as "founders" has been known for a long time. The condition occurs in horses after they have eaten large amounts of grain. The characteristic symptoms of the disease are muscle tremors, anorexia, increased respiratory rate, lesions of the hoof, fever, and frequently death. The physiological disturbances characteristic of the condition have been investigated by Åkerblom[1] who found it possible to reproduce the disease by the administration of 10 g. of histidine together with a culture of *Bacillus coli.* The *B. coli* apparently decarboxylate the histidine to form histamine which was found in the gastrointestinal contents of affected horses. Typical symptoms of the disease could be produced by the intravenous or subcutaneous administration of histamine. The disease appears to be due to the absorption of histamine which arises from the histidine of the ingested grains. The formation of histamine is apparently dependent on the action of microorganisms in the gastrointestinal tract.

FEEDS FOR HORSES

Pasture. The natural feed and best source of nutrients for horses is pasture. With the addition of limited amounts of concentrates for foals, brood mares, and horses at hard work, good pasture provides all the nutrients horses need. Not only is it the least expensive feed for horses, but its use involves a minimum of labor. Horses worked throughout the day should be pastured at night during hot weather not only for the sake of economy, but because they are more thrifty on pasture and cooler there than in stalls. While blue-grass or other permanent pasture is excellent for use in early spring and fall, a mixture of grass and legumes is superior to grass alone.

Unlike ruminants, horses are likely to consume more roughage than they can handle, because the comparatively small stomach of the horse limits its capacity. Digestive disturbances are likely to result from a digestive tract unduly distended with roughage, especially when the horse is working hard. For horses doing hard work, the amount of hay fed should be sharply limited, especially if it is palatable, and it should be fed mostly at night when the animal has sufficient time for its mastication and digestion.

The maximum amount of hay usually allowed a work horse is 1 to 1½ pounds of hay per 100 pounds of live weight, while the minimum amount of roughage required has been shown by experimental work to be as low as ⅔ of a pound of hay per 100 pounds of body weight. The total dry matter fed a 1000-pound working horse can be as little as 15 or as much as 22 pounds, while an idle horse of this same weight can safely be fed as little as 12 pounds of dry matter. Since individual variations in stomach capacity exist, it is necessary to observe the individuals carefully to make sure that each is receiving enough, and not too much, roughage.

Timothy hay is considered the standard roughage for horses in the northern part of the United States and in eastern Canada, and since the protein content of timothy hay is relatively low, it must be supplemented with concentrates when fed to foals and brood mares. In the western part of the United States, cereal hays, about equal to timothy hay as horse feed, are used extensively. Corn fodder and corn stover, if of good quality, are nearly equal in feed value to timothy hay for horses.

The widespread prejudice against legume hay for horses is not well founded but seems to be based partly on the fact that, when it is fed in unlimited amounts, horses will gorge themselves on it, and partly on the fact that legume hay of poor quality actually is harmful and should not be used. Legume hay, more concentrated than timothy, should be fed in smaller amounts than the latter.

Straw can be used successfully as a feed for idle horses provided some concentrate is fed with it, but it is considered unsuitable for horses at hard work because of its low energy value as a feed.

Concentrates. Oats are considered almost an ideal feed for horses. They are less concentrated than other grains due to their bulky hulls, and they form a loose mass in the stomach while other feeds tend to pack. Oats are less likely than other concentrates to cause trouble if the horse has an opportunity to gorge himself. On the other hand, when corn or barley is cheaper than oats, these concentrates can be used with entirely satisfactory results. No matter what feed is given to horses, it must be of good quality because horses are especially susceptible to injury from damaged feeds.

BIBLIOGRAPHY

1. Åkerblom, E., *Skand. Arch. Physiol.* (Suppl.) **68**: 1 (1934).
2. Bennetts, H. W., and Beck, A. B., *Austral. Council Sci. Indust. Res. Bull.* **147** (1942).
3. Brody, S., "Bioenergetics and Growth." New York, Reinhold Publishing Corp. (1945).
4. Brody, S., Kibler, H. H., and Trowbridge, E. A., *Univ. Mo. Agr. Expt. Sta. Res. Bull.* **368** (1943).
5. Callender, G. R., and Kelser, R. A., *Am. J. Path.* **14**: 253 (1938).
6. Carlstrom, B., and Hjarre, A., *Biedermann's Zentr. B. Tierernahr.* **11**: 121 (1939).

7. Carlstrom, B., and Hjarre, A., *Skand. Vet. Tidskr.* **28**: 518 (1938).
8. Davis, G. K., and Cole, C. L., *J. Animal Sci.* **2**: 53 (1943).
9. Dinsmore, Wayne, Secretary, Horse and Mule Assoc. of Am., personal communication (1947).
10. DuBois, K. P., Moxon, A. L., and Olson, O. E., *J. Nutrition* **19**: 477 (1940).
11. Earle, I. P., Letter to the authors (1948).
12. Filmer, J. F., *Aust. Vet. J.* **9**: 163 (1933).
13. Forbes, W. H., *Milbank Mem. Fund Quart.* **23**: 89 (1945).
14. Griem, W. B., Hart, E. B., Kalkus, J. W., and Welch, H., *Nat'l. Res. Council Reprint* and *Circ. Ser.* **111** (1942).
15. Guilbert, H. R., Howell, C. E., and Hart, G. H., *J. Nutrition* **19**: 91 (1940).
16. Hart, G. H., Goss, H., and Guilbert, H. R., *Am. J. Vet. Res.* **4**: 162 (1943).
17. Harvey, A. L., Palmer, L. S., Kernkamp, H. C. H., Nelson, J. W., and Olson, F. C., Paper presented 37th Ann. Meeting Am. Soc. Animal Prod. (1944).
18. Harvey, A. L., Thomas, B. H., Culbertson, C. C., and Collins, E. V., *J. Animal Sci.* **2**: 103 (1943).
19. Harvey, A. L., Thomas, B. H., Culbertson, C. C., and Collins, E. V., *Proc. Am. Soc. Animal Prod.* **32**: 94 (1939).
20. Hill, A. V., "Muscular Movements in Man," pp. 30–32. New York, McGraw-Hill Book Co., Inc (1927).
21. Howell, C. E., Hart, G. H., and Ittner, N. R., *Am. J. Vet. Res.* **2**: 60 (1941).
22. Hudson, R. S., *Mich. Quart. Bull.* **8**: 103 (1926).
23. Huff, J. W., Pearson, P. B., and Perlzweig, W. A., *Arch. Biochem.* **9**: 99 (1946).
24. Jones, T. C., *Mil. Surgeon* **96**: 310 (1945).
25. Jones, T. C., Roby, T. O., and Maurer, F. D., *Am. J. Vet. Res.* **7**: 403 (1946).
26. Kintner, J. H., and Holt, R. L., *Philippine J. Sci.* **49**: 1 (1932).
27. Kleiber, M., *Physiol. Rev.* **27**: 511 (1947).
28. Klemola, V., *Die Tierernahrung* **5**: 657 (1933).
29. Lane, A. H., *S. African Vet. J., N.S.* **13**: 232 (1906).
30. Law, James, "Textbook of Veterinary Medicine." 3rd ed. Ithaca, New York, Published by author (1911).
31. Madison, T. C., Sanitary Rept. Fort Randall, in Coolidge, R. H. A Statistical Rept. on the Sickness and Mortality in the Army of the United States, January 1855 to January 1860, Washington, D. C., G. W. Bowman, *1860 (U. S.) Cong. 36th, 1st Session, Senate Ex. Doc.* **5237–41**: 1860.
32. McCance, R. A., *Lancet* **1**: 765, 823 (1936).
33. Mitchell, H. H., *J. Animal Sci.* **6**: 365 (1947).
34. Mitchell, H. H., Letter to the authors (1947).
35. Mitchell, H. H., *Am. Soc. Animal Proc. 26th Ann. Meeting* **1933**, 229; and personal communications.
36. Morrison, F. B., "Feeds and Feeding." Ithaca, New York, The Morrison Publishing Co., 1948.
37. Moulton, C. R., *J. Biol. Chem.* **57**: 79 (1923).
38. Moxon, A. L., *So. Dakota Agr. Expt. Sta. Bull.* **311** (1937).
39. Moxon, A. L., and Rhian, M., *Physiol. Rev.* **23**: 305 (1943).
40. Naito, K., Shimanura, T., and Kuwabara, K., *3rd Rept. Jap. Gov't Inst. for Vet. Res.*, p. 51, 1925.
41. Nitsche, H., *Biedermann's Zentr. B. Tierernahr.* **11**: 214 (1939).
42. Nurni, K., *J. Jap. Soc. Vet. Sci.* **6**: 273 (1927).
43. Nurni, K., and Aoki, M., *Trop. Vet. Bull.* **16**: 70 (1928).
44. Pearson, P. B., *J. Biol. Chem.* **106**: 1 (1934).

45. Pearson, P. B., *J. Dairy Sci.* **30**: 73 (1947).
46. Pearson, P. B., and Luecke, R. W., *Arch. Biochem.* **6**: 63 (1945).
47. Pearson, P. B., and Schmidt, H., *J. Animal Sci.* **7**: 78 (1948).
48. Pearson, P. B., Sheybani, M. K., and Schmidt, H., *J. Animal Sci.* **2**: 175 (1943).
49. Pearson, P. B., Sheybani, M. K., and Schmidt, H., *J. Animal Sci.* **3**: 166 (1944).
50. Pearson, P. B., Sheybani, M. K., and Schmidt, H., *Arch. Biochem.* **3**: 467 (1944).
51. Schmidt, H., Unpublished data.
52. Schweigert, B. S., Pearson, P. B., and Wilkening, M. C., *Arch. Biochem.* **12**: 139 (1947).
53. Sturgess, G. W., and Crawford, M., Administrative Rept. of Gov't. Vet. Surgeon, Ceylon (1927).
54. Templeton, G. S., *Miss. Agr. Expt. Sta. Ann. Rept.* 1928, p. 18.
55. Terroine, F., and Reichert, T., *Compt. rend. Acad. Sci.* **190**: 768 (1930).
56. Vogt-Moller, P., "Vitamin E—A Symposium," pp. 57–66, Cambridge, England, W. Heffer and Sons Ltd. (1939).
57. Winchester, C. F., *Science* **97**: 24 (1943).

Chapter XVI

THE NUTRITION OF SHEEP AND GOATS

P. B. Pearson

U. S. Atomic Energy Commission, Washington, D. C., and
Animal Husbandry Division, Bureau of Animal Industry, U. S. Department
of Agriculture, Beltsville, Maryland

Sheep. The center of sheep production in the United States is in the western states where a high proportion of the land is not suitable for cultivation. More than any other domestic animal, sheep depend upon grass as their only or major source of feed. The feeding of mixed rations, cured forages and grains is of secondary importance in the over-all production of sheep in this country. The efficiency of sheep in converting feeds into edible food for human consumption is approximately the same as for cattle but is somewhat less than for poultry or pigs.[38] Making appropriate allowance for the value of wool and edible meat combined, sheep appear to be somewhat more efficient than cattle in converting feeds into consumable products of economic importance for mankind. The importance of sheep in our economic structure is more apparent when it is kept in mind that a large proportion of their food supply does not enter into competition with the human food supply. When crops, such as our cereal grains, are fed to animals instead of being eaten directly by human beings, they lose 80 to 90 per cent of their calorie value before they are transformed into meat, milk, and eggs. In contrast to pigs and poultry, sheep consume large amounts of roughage, pasture grass, and fibrous byproducts inedible by man. Furthermore, over the vast range areas of the Southwest and Western states their production is centered in areas that are not suitable to cultivation; consequently the utilization of these areas for food production is dependent to a very large extent on herbivorous animals.

The economical and efficient production of sheep and wool is contingent upon adequate nutrition. Nutritional deficiencies generally reduce the efficiency of food utilization and impair the production capacity of the animal. The nutrition of the ewe during gestation largely determines the growth and development of the fetus, and strong vigorous lambs at birth are one of the first essentials in successful sheep production. Hammond [illegible] and Verges[67] have shown that when ewes were full fed during the last third of the gestation period, the twin lambs from these ewes were 47 per cent heavier at birth than lambs from similar ewes that were fed only slightly above maintenance requirements. The difference was less marked in the case of single lambs where the nutritive requirements are naturally somewhat lower. Proper nutrition during gestation also results in increased milk flow and more rapid growth of the lamb.

Goats. Angora goats are raised primarily for the production of mohair. However, along the border between the United States and Mexico, there is considerable demand for goats for human food. While a large proportion of the Anogra goats in this country are raised on fenced ranges of the Edwards Plateau in southwestern Texas, they are also fairly important in several other states including Arizona, New Mexico, Oregon, California, and Missouri.

Angora goats obtain most of their feed on the range in the form of grass, browse, and weeds. During the winter they are frequently forced to subsist to a large extent on evergreen shrubs and bushes. When supplemental feed is necessary, cottonseed meal, corn, milo, oats, and similar feeds can be used.

There is virtually no experimental information on which to base the nutritional requirements of Angora goats. In the absence of precise information for the goat and on the basis of practical experience and observations it appears that the nutritional requirements of Angora goats would be satisfied by using as a guide the allowances recommended for sheep. The nutritional requirements of milch goats are similar to those of dairy cows. (See Chapter XIII.)

NUTRIENT ALLOWANCES

In 1949 the National Research Council Committee on Animal Nutrition published the report on "Recommended Nutrient Allowances for Sheep."[46] This report was prepared by a group of nutritionists who have devoted special attention to the nutrition of the sheep. Much of the data in Table 101 on the quantitative requirements of sheep for various nutrients follows the recommendations of the Committee on Animal Nutrition of the National Research Council.

There is a wide difference in the size of sheep at maturity and in their rate of development. Naturally the protein requirement for a 60-pound lamb of one of the larger breeds such as the Hampshire would be more than for a Southdown lamb of the same weight. The nutrient allowances in Table 101 allow a margin of safety for variation in quality of feeds, climatic conditions and are calculated to provide sufficient nutrients for the common breeds of sheep and for Angora goats.

Protein. Protein is of special importance for the young growing animal and for pregnant and lactating ewes. On the basis of weight increase and nutrient requirements, development of the fetus occurs at an increasing rate with the advance of the gestation period. In fact most of the growth takes place during the last third of the gestation period. The nutrients stored in the fetus consist largely of protein. Approximately two-thirds of the new-born lamb on a dry basis is protein with the remaining one-third consisting chiefly of fat and minerals. During the first few weeks of life after birth, the lamb's food consists almost entirely of milk which is relatively high in protein. This high proportion of protein in the diet of the young lamb is closely connected with the development of new body tissues that are high in protein. As the animal grows, relatively smaller amounts of protein and larger amounts of fat are deposited.

TABLE 101. DAILY ALLOWANCES FOR SHEEP

Live Weight lb.	Expected Daily Gain or Loss lb.	Total Feed Air Dry Basis lb.	Total Digestible Protein		Total Digestible Nutrients		Calcium Intake		Phosphorus Intake		Salt lb.	Carotene Intake mg.
			In Ration %	Per Sheep lb.	In Ration %	Per Sheep lb.	In Ration g.	90% Dry Matter %	In Ration g.	90% Dry Matter %		
BRED EWES FIRST 100 DAYS OF GESTATION												
100	0.12	3.5	5.0	0.17	50	1.7	3.2	0.20	2.5	0.16	0.03	5.5
110	0.12	3.6	5.0	0.18	50	1.8	3.2	0.20	2.6	0.16	0.03	6.0
120	0.12	3.7	5.0	0.19	50	1.9	3.3	0.20	2.7	0.16	0.03	6.5
130	0.12	3.8	5.0	0.20	50	2.0	3.4	0.20	2.7	0.16	0.03	7.0
BRED EWES LAST 6 WEEKS BEFORE LAMBING												
110	0.25	4.0	5.0	0.21	53	2.1	4.3	0.24	3.2	0.18	0.03	6.0
120	0.25	4.1	5.0	0.22	54	2.2	4.4	0.24	3.3	0.18	0.03	6.5
130	0.25	4.2	5.0	0.23	54	2.3	4.5	0.24	3.4	0.18	0.03	7.0
140	0.25	4.3	5.0	0.24	55	2.4	4.7	0.24	3.5	0.18	0.03	7.5
150	0.25	4.4	5.0	0.25	55	2.5	4.8	0.24	3.6	0.18	0.03	8.0
EWES IN LACTATION												
100	-0.10	4.5	6.0	0.27	58	2.5	6.1	0.30	4.5	0.22	0.03	6.0
110	-0.10	4.6	6.0	0.28	58	2.6	6.2	0.30	4.6	0.22	0.03	7.1
120	-0.10	4.7	6.0	0.28	58	2.7	6.4	0.30	4.7	0.22	0.03	7.8
130	-0.10	4.8	6.2	0.30	58	2.8	6.5	0.30	4.8	0.22	0.03	8.4
140	-0.10	4.9	6.1	0.30	58	2.9	6.6	0.30	4.9	0.22	0.03	9.1
150	-0.10	5.0	6.1	0.31	58	3.0	6.8	0.30	5.0	0.22	0.03	9.7
EWES -- LAMBS AND YEARLINGS												
70	0.35	3.0	7.3	0.22	58	1.8	3.0	0.22	2.7	0.20	0.02	3.8
90	0.30	3.2	6.9	0.22	58	1.9	3.0	0.21	2.7	0.19	0.02	5.0
110	0.20	3.5	5.7	0.20	54	1.9	3.2	0.20	2.8	0.18	0.03	6.0
130	0.10	3.8	5.3	0.20	54	2.0	3.1	0.18	2.7	0.16	0.03	7.1
RAMS -- LAMBS AND YEARLINGS												
75	0.45	3.5	6.8	0.24	58	2.1	3.8	0.24	3.2	0.20	0.02	4.1
100	0.40	4.0	6.0	0.24	60	2.3	4.0	0.22	3.4	0.19	0.03	5.5
125	0.35	4.0	6.0	0.24	60	2.4	3.6	0.20	3.3	0.18	0.03	6.9
150	0.30	4.3	5.3	0.23	60	2.6	3.7	0.19	3.3	0.17	0.03	8.2
175	0.20	4.5	5.1	0.23	58	2.6	3.7	0.18	3.3	0.16	0.03	9.6
FATTENING LAMBS												
50	0.25	2.1	8.1	0.17	57	1.2	2.5	0.26	2.1	0.22	0.02	2.7
60	0.30	2.3	7.8	0.18	60	1.4	2.6	0.25	2.2	0.21	0.02	3.3
70	0.35	2.7	7.0	0.19	63	1.7	2.9	0.24	2.4	0.20	0.02	3.8
80	0.35	2.9	6.9	0.20	65	1.9	2.9	0.22	2.4	0.18	0.02	4.4
90	0.25	3.0	6.7	0.20	66	2.0	2.7	0.20	2.3	0.17	0.02	5.0

Wool and mohair belong to a class of proteins known as keratins. (See Chapter III, Volume I.) The keratins as a class of proteins are resistant to the action of the digestive enzymes and are relatively high in sulfur-containing amino acids and in the hexone bases. A sheep producing

8.5 pounds of wool annually (equivalent to 5 g. of clean wool daily) requires some extra protein for this function.

The low level of sulfur-containing amino acids in herbage led Martson and Robertson [37] to postulate that cystine might be a limiting factor in the production of wool. This theory and the work of Marston [33, 34] have not been entirely substantiated by more recent workers. That the quality of wool grown may, within certain limits, be influenced by the level of protein in the ration seems fairly well established.[35]

The bacteria present in the rumen of polygastric animals play a special role in the nutrition of ruminants such as sheep and goats. Nonprotein forms of nitrogen such as that in urea, amides, and ammonium carbonate can be converted into protein by bacteria in the rumen. The proteins thus synthesized are built into the body proteins of the microorganisms. They are then digested further down the digestive tract and are added to the supply available for the physiological needs of the host animal. Harris and Mitchell [22] demonstrated that protein formed by microorganisms is available to sheep for maintenance and growth purposes. They found that the biological value of urea nitrogen was approximately 22 per cent less than the biological value of a good quality protein supplement. From the work of Hamilton, Robinson and Johnson,[20] it appears that urea is a satisfactory source of nitrogen for growing lambs provided at least 25 per cent of the food nitrogen is in the form of preformed protein and that the total protein equivalent of the ration does not exceed about 12 per cent. Under practical feed lot trials, urea has not proved to be entirely satisfactory when added to low protein rations.[7, 70] It now appears that the unfavorable results obtained with urea may be corrected by adding methionine to a low protein ration containing urea. Loosli and Harris [30] have shown that the addition of methionine to a low-protein ration containing urea resulted in essentially as good gains by lambs as where linseed meal was fed.

The protein allowances shown in Table 101 have been arrived at after a consideration of feeding experiments, balance studies and other criteria for measuring protein requirements. Allowance is made to meet the needs for wool and milk production. It may be desirable to feed slightly higher amounts to ewes in poor condition and ewes nursing twin lambs.

Energy and Carbohydrate. The major components of herbage and cereal grains are the carbohydrates. The carbohydrates are, under normal conditions, the most economical source of energy for the animal. The energy requirements are a matter of considerable importance since there are periods during the year when production is, to a considerable extent, limited to growth of wool and the fetus. In the growing animal the energy requirements vary with the stage of development. According to Peirce [48] suckling Merino lambs, aged 3 to 12 days, have a standard metabolism of 1890 calories per M^2 per 24 hours as compared with 1310 calories for lambs 96 to 114 days of age.

The fiber content of common roughage makes up about 30 per cent of the total dry matter. Since sheep depend to a very large extent on herbage, the extent that they are able to utilize the fiber in roughages is very important. Ruminants have more ability to digest and utilize fiber than monogastric animals. They do not digest the fiber in all feeding stuffs to an equal extent. The fiber in young green plants is digested much more completely than the fiber in plants that have matured and reached the seed stage. As the plant matures, the cellulose portion of the fiber becomes lignified. Lignin is almost entirely undigestible even by ruminants. With lignification there is a decrease in the digestibility of the nitrogen-free extract, protein, and fat. This is very well illustrated by Woodman[72] who found that in young leafy grass the digestive coefficients were for the fiber 84, nitrogen-free extract 87, protein 85, and fat 60, while for similar grass at the hay stage of maturity the corresponding digestion coefficients were 52, 53, 50 and 30.

The energy value of feedstuffs for the animal is not constant, but varies with the plane of nutrition and other factors. The total digestible nutrients is the sum of the digestible protein, digestible fiber, digestible nitrogen-free extract and digestible fat multiplied by 2.25. The extent to which the animal utilizes the digestible nutrients for maintenance or production purposes is not constant even with single feeds. The requirements as given in Table 101 allow for variation in the ability of the animal to utilize the nutrients and in the composition of feeds. They are in accord with numerous feeding experiments.

VITAMINS

Carotene. Existing evidence indicates that vitamin A is the most likely of the known accessory organic food factors to occur in amounts such as to limit the nutritional well-being of sheep. Carotene is the precursor of vitamin A (see Chapter XXI, Volume I) and is the form in which this factor occurs in natural feeds consumed by sheep. When there is an abundance of good quality green grass, the intake of carotene is greatly in excess of the immediate needs of the animal. The animal has the ability to store relatively large amounts of vitamin A principally in the liver. The vitamin A reserve of sheep that have been on good green grass during the spring and summer is normally sufficient to take care of the needs of the animal during the autumn and winter months when the intake of carotene is restricted.

The concentration of carotene in herbage tends to decrease as plants approach maturity and by the time they are dry only small amounts of carotene remain. During dry years sheep store very little vitamin A; consequently, they have little or no reserve to carry them through the autumn and winter months when the feed, especially in the range areas, provides only small amounts of carotene. Under these conditions or where lambs are fattened on rations lacking in good quality silage or hay, a vitamin A deficiency is most likely to occur. Consideration of this is important since the period of pregnancy of sheep under most systems of management is during the fall and winter months. Lambs and kids from ewes and goats maintained under normal conditions are born with little or no reserve of vitamin A in the liver and must depend for the first few weeks of life on the vitamin A supplied by the mother's milk.[61] A deficiency of vitamin A adversely affects reproduction, and may result in lambs born dead or weak. (See Figure 33.) Underwood and Curnow[64] found that in seasons when the ewes had access to young green grass during the last two months of gestation the vitamin A potency of the colostrum was more than double the value during the years there was no green grass for grazing. Within 48 hours after parturition the vitamin A potency of the milk may decrease to one-tenth the level in the first colostrum.

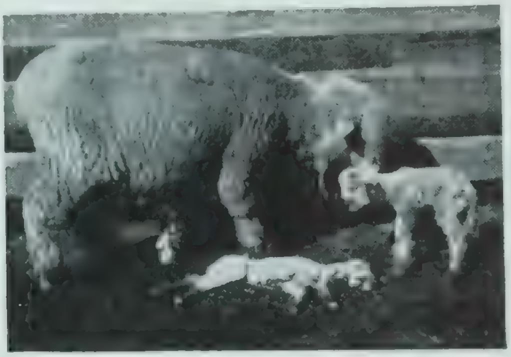


FIG. 33. The effect on reproduction of feeding a ration low in vitamin A. One lamb was born dead and the other died six weeks after birth. (Courtesy of the Calif. Agr. Expt. Sta.)

One of the first symptoms of vitamin A deficiency is night blindness or inability to see in dim light. Later, muscular incoordination occurs followed by anorexia with a subsequent loss of weight. Sheep may develop night blindness and continue to grow normally for several months.[50, 54] The vitamin A content of the blood affords a good indication of a state of vitamin A deficiency in sheep. Peirce[50] observed that sheep fed rations providing only 10 micrograms of carotene per kilogram of body weight showed very little decline in blood plasma level from the original 35 micrograms per 100 ml. for the first three months. At six months the level had fallen to 23 micrograms, and it was only after 13 months that a constant level of 6 micrograms of vitamin A per 100 ml. of plasma was reached. Night blindness occurred when the level reached 25 to 20 micrograms per 100 ml. of plasma. The level in blood may be maintained at a nearly normal value even with a low concentration of vitamin A in the liver. A level in the blood of 20 micrograms or less per 100 ml. of plasma definitely indicates that the liver reserve has been depleted and that a deficiency state exists.

The carotene requirements of sheep are similar to the requirements of other species[19] and vary from 25 to 35 micrograms per kilogram of body weight. This amount does not allow for storage, reproduction, and other special needs. The National Research Council Committee report recommends that practical rations for sheep provide about four times the minimum level. This should insure an adequate level for reproduction, lactation, and other special needs.

Vitamin D. The metabolism and utilization of calcium and phosphorus for the development of skeletal structures is the primary function of vitamin D. Under range conditions where sheep have little protection from the elements of the weather, there is probably adequate ultraviolet irradiation to transform sufficient of the 7-dehydrocholesterol into active vitamin D_3 to provide for the needs of sheep for this vitamin. Where sheep are confined or exposure to sunshine is restricted due to other conditions, lambs may develop rickets due to an insufficient amount of vitamin D. It has been shown experimentally that lambs fed a ration low in vitamin D and not exposed to sunshine develop rickets[2, 10] and similar conditions have been observed in lambs under feed-lot conditions.

The symptoms that may be observed in vitamin D deficiency in sheep are enlargement of the joints and bowing of the legs in the immature animal, stiffness in the anterior or posterior quarters and an irregular gait. The joints may be very painful, and the lamb frequently carries or drags one limb.

Information on the quantitative requirements of sheep is not available. A figure of 6.6 I.U. of vitamin D per kilogram of body weight was proposed for calves by Bechdel et al.[3] On the basis of available information, this figure would probably meet the requirements for sheep and Angora goats where an extra source of vitamin D is indicated.

Vitamin E. The most outstanding characteristic of experimental vitamin E deficiency is the multiplicity of structural and functional alterations manifested by various species. There is no experimental evidence that reproductive difficulties in sheep or goats are due to a lack of vitamin E in the diet. Thomas and associates[59] fed goats a diet that was so deficient in vitamin E that it did not permit reproduction in rats. Goats on this ration were carried through the third generation without any impairment in reproduction. The effect of liberal supplementation with wheat-germ oil as a source of vitamin E on reproduction was studied over a two-year period using 99 pairs of matched ewes of various breeds.[60]

There was no consistent difference in the reproductive performance of the ewes receiving wheat-germ oil and those not fed the supplement.

In the sheep a deficiency of vitamin E is manifested as a type of muscular dystrophy commonly referred to as "stiff-lamb disease." The condition may be encountered in lambs either under range condition or in dry lot. The relation of vitamin E or tocopherol to nutritional muscular dystrophy was first obsereved in guinea pigs and rabbits [16] and has since been reported in a number of other species. The lesions in affected lambs appear as whitish areas in the muscle. The striated musculature is most commonly affected, but occasionally there are heart lesions which appear as white patches under the endocardium. In some cases intramuscular hemorrhages are encountered. This is probably due to a dysfunction of the vascular system, a common manifestation of the deficiency in some species. Willman et al.[69] showed that either wheat-germ oil or tocopherols are effective in preventing or curing muscular stiffness in lambs. On the basis of this work, it appears that the requirement of lambs for vitamin E is met by about 2 mg. of mixed tocopherol daily per kilogram of body weight.

The fact that lambs may develop a vitamin E deficiency while on natural feeds does not seem to be explained entirely by the fact that feeds consumed are low in tocopherols. The most plausible explanation is that the naturally occuring tocopherols ingested in plant materials undergo some destruction probably during rumination and passage through the large sectional stomach,[23] making it necessary to ingest larger quantities. The muscular dystrophy produced by the Cornell workers [32] by feeding cod liver oil to sheep and goats now appears to have been due to a deficiency of vitamin E brought about in the gastro-intestinal tract by the destruction of the tocopherols due to the action of some constituent in the cod liver oil.

B Vitamins. The first report indicating that the B vitamins may not be dietary essentials for sheep was made by Winegar, Pearson and Schmidt.[71] Lambs fed a ration low in nicotinic acid during an eight-month period developed normally. This, together with data on the urinary excretion of nicotinic acid, led these workers to conclude that this vitamin is not a dietary essential for the sheep. The interpretation of these results may be in some doubt since it is now known that in at least some herbivora (rabbit and horse) the major end product of nicotinic acid metabolism is N′-methylnicotinamide and not nicotinic acid. Furthermore it has been shown that dietary tryptophan can be converted in vitro to nicotinic acid.[53, 55] Thus the level of dietary tryptophan may be a factor in the quantitative requirements of the animal for nicotinic acid.

McElroy and Goss [39] have shown that even where sheep are fed a ration low in thiamine, riboflavin, pyridoxine, pantothenic acid, and vitamin K, there is a considerable synthesis of all of these factors in the rumen. Recently it has been shown that even in the newborn calf nicotinic acid is not a dietary essential for the growth of this species.[27] The available data indicate that with sheep old enough to have developed functional rumens to provide for microbiol-synthesis, at least the first five members of the B vitamins are not dietary essentials.

There is reason to believe that the newborn lamb for the first few weeks of life may have definite requirements for a source of some of the B vitamins. It has recently been found that on a riboflavin deficient diet the calf develops definite pathological symptoms and that riboflavin practically disappears from the urine.[68] As a corollary it would follow that the newborn lamb would probably require a dietary source of riboflavin.

Further evidence that a source of dietary riboflavin may be needed by the newborn lamb may be adduced from the high riboflavin content of ewe's colostrum.[47] The colostrum of the ewe contains about 20 micrograms of riboflavin per milliliter, whereas the milk contains an average of 4.4 micrograms per milliliter. In contrast, the nicotinic acid and pantothenic acid contents of the colostrum were not significantly higher than in the milk. There was some difference in the thiamine content but it was of a much smaller order than in the case of riboflavin.

MINERALS

Several mineral elements including phosphorus, calcium, iodine, copper, and cobalt are known to be essential for vital functions of sheep, and on the basis of investigations with other species, it would be expected that manganese, magnesium, sodium, and possibly other elements are also essential. In contrast to the essential mineral elements there are at least two mineral elements, namely fluorine and selenium, that may occur in feedstuffs in amounts sufficient to be toxic. In many parts of the world, areas where specific mineral deficiencies occur have been fairly well mapped.

Calcium and Phosphorus. These two elements are discussed together because they serve similar functions in the skeletal structures of the body. In the soft tissues of the body they serve quite different functions. Over 70 per cent of the ash of the body consists of these two elements, and of the total calcium content of the body over 99 per cent occurs in the skeletal structures. Phosphorus is more widely distributed in the soft tissues of the body as only about 80 per cent of the total amount in the body occurs in the bones and teeth.

Phosphorus participates in the metabolism of carbohydrates, fats, and proteins. It is known that the various phosphorylations which occur during dissimilation of carbohydrate are the means by which the energy liberated from oxidative steps is prevented from being dissipated as heat and is held or built up in the body for productive purposes.[31] The recent work of Rittenberg and Shemin[52] indicates that the synthesis of body protein from absorbed amino acids involves a phosphorylation process. This is supported by the results of Morris and Ray[42] showing that a phosphorus deficiency depresses the biological value of the protein component of the ration for sheep.

The skeletal reserve of calcium appears to be more readily mobilized than the phosphorus. The hormone from the parathyroid gland aids in maintaining the calcium content of the blood by withdrawing the calcium from the bones.

The feeding of rations that are deficient in phosophorus results in subnormal development, high feed requirement, depressed appetite, general unthrifty appearance, anorexia, and low blood inorganic phosphorus values. Aphosphorosis in ewes causes weak lambs and decreased milk production. Herbage having a low phosphorus content and reflecting either a low phosphorus content of the soil or unavailability of the phosphorus occurs in many sections of the world.

A lack of calcium in the diet is known to affect reproduction adversely. Fraser, Godden and Thomson[14] fed pregnant ewes a ration that provided only 1.12 g. of calcium daily. These ewes were in a negative calcium balance, developed hypocalcemia, anorexia, incoordination, staggering, weakness of the legs, tonic and colonic convulsions, and paralysis.

A deficiency of calcium may occur in rations in which the roughage consists of sorghum silage, sorghum fodder or corn silage and the cereal grains or their by-products. Such rations should be supplemented with 0.5 to 1 per cent of calcium carbonate or limestone.[29, 70]

There is considerable variation in the levels of calcium and phosphorus recommended for sheep by various investigators. Mitchell[41] estimates that the calcium requirements for growing lambs would be met by 0.18 per cent in the ration expressed on a dry basis while the recommendations of the National Research Council Committee on Animal Nutrition are slightly higher. Likewise the requirements for phosphorus as estimated by Mitchell are 0.15 per cent while the National Research Council Committee Report recommends a slightly higher level. The availability of phosphorus in natural feedstuffs would influence the amount necessary to provide in the ration. A deficiency of phosphorus is most likely to occur during dry seasons and periods when the feed is restricted chiefly to herbage that has been allowed to reach maturity. The per cent of phosphorus on a dry weight basis tends to decrease as plants mature. High protein feeds, such as cottonseed meal, which is used extensively in the southwest as a supplemental feed for range sheep, and soybean meal, are relatively rich in phosphorus.

Iodine. The amount of iodine present in the animal body is extremely small, probably less than 1.8 g. in a 100-pound sheep. This small amount of iodine is essential for reproduction and normal physiological processes. In extensive sections of the world and especially in the high mountainous regions, the soils, plants grown thereon, and the water are very low in iodine. The iodine-deficient areas in the United States include sections of the states of Wisconsin, Ohio, Iowa, Indiana, Illinois, Michigan, Montana, Nebraska, New York, the Dakotas, Utah, Nevada, Colorado, Idaho, Oregon, California, and Washington.

Iodine exerts its physiological effects through the thyroid glands as the hormone thyroxine. Removal of the thyroid gland in the young animal results in a stunting of the normal physiological development. Visible evidences of iodine deficiency occur most frequently in newborn lambs. The most characteristic manifestation of an iodine deficiency is goiter or enlargement of the thyroid gland (Figure 34). Lambs are frequently dead at birth or die soon afterward. It is known that before the feeding of iodine was practiced serious losses of lambs occurred in the iodine-deficient belt of the United States and Canada.

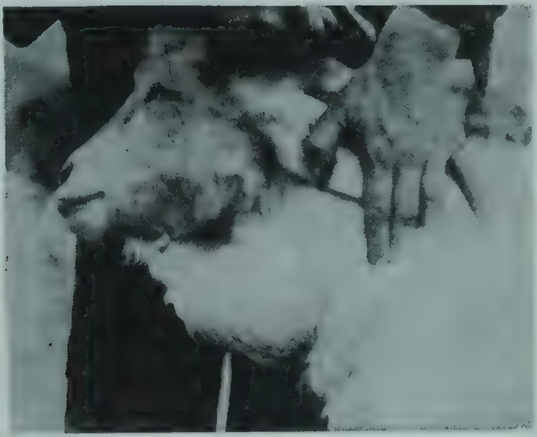


FIG. 34. Simple hyperplastic goiter in adult Angora goat due to a deficiency of iodine. (Courtesy of the Western Wash. Agr. Expt. Sta.)

The most effective means of supplying iodine to sheep in proper amounts is through the salt. The iodine requirements of various species have been reviewed by Griem et al.[17] On the basis of the recommendation of the Study Committee on Endemic Goiter of the American Public Health Association, iodized salt is now formulated with one part of potassium iodide in 10,000 parts of salt. This is 0.01 per cent of potassium iodide or 0.0076 per cent iodine. The feeding of salt iodized at this level would normally furnish several times the iodine requirements for sheep.

Iron and Copper. Iron plays a vital role in life processes as it is a constituent of heme which makes up about 4 per cent of the hemoglobin molecule. In the absence of an adequate amount of iron the rate of formation of red blood cells fails to keep pace with the rate of destruction, thereby resulting in anemia. Nutritional anemia due to an iron deficiency does not occur under practical conditions of sheep production. So far as known there is no naturally occurring deficiency of iron in rations for sheep in any part of the world.

It is now well established that small amounts of copper are necessary for the utilization of iron in the formation of hemoglobin. There are areas in the world where there is a deficiency of copper in herbage making it necessary to supply additional copper for successful sheep production.

In parts of South Australia a disease of sheep known as "coast disease" was shown by Marston and McDonald [36] in 1938 to respond to copper and cobalt, although the latter now appears to be the dominant deficiency. A deficiency of copper also occurs in certain sections of Florida. Here most of the work has been with cattle. In 1940 Innes and Shearer [25] gave a detailed description of an endemic disease encountered in lambs in England, Scotland, and Wales. The disease was referred to as "swayback" and the incidence was found to run as high as 90 per cent. These workers suggested that the disease might be due to a deficiency of copper.

In sections of Western Australia the copper content of the herbage is so low that supplementation is necessary for successful sheep production. The condition referred to as enzootic ataxia has been described in detail by Bennetts and Beck.[5] Prior to the discovery that the condition was due to a deficiency of copper, the practice was to move the ewes during the gestation period from the affected areas to "sound" country, or to purchase each year new breeding stock from healthy areas.

Enzootic ataxia is confined to lambs of ewes that have been pastured for several months on areas deficient in copper. Affected lambs may be born dead, or be affected at any age up to four months with the highest incidence from one to two months of age. In general the incidence seems to be highest among the rapidly growing and fattening lambs. The first evidence of the disease is unthriftiness and decrease in growth rate. Lambs in this early stage, when driven a distance of from one-half mile to a mile, develop an incoordination of gait affecting particularly the hind limbs. The condition progresses within a few days to where the ataxia is manifest after the animal has been driven only a short distance. According to Bennetts and Beck,[5] "The hind legs are drawn up together when the lambs run, the limbs are excessively flexed and knuckle over at the pasterns, the gait shows incoordination of movement, the hind quarters wobble and ultimately sway to one side and the lamb falls over." (See Figure 35.) In the more advanced stage the forelegs are also affected. Appetite is maintained, but the animal is generally unable to obtain much food. The condition becomes worse and in most cases the lamb dies within three or four weeks from malnutrition or infections that develop due to the weakened condition.

Lambs that have been affected with the disease for a few weeks are usually anemic. The chief lesions of ataxia occur in the nervous system. Here there is a degeneration of the myelin sheaths of the nerve fibers of the spinal cord. The copper content of the blood of affected lambs or ewes that gave birth to affected lambs was less than one-fifth of the value for healthy animals. While the blood copper level of healthy animals nearly always exceeded 50 micrograms per cent, affected animals generally had values as low as 10 or 20 micrograms per cent. Likewise, the copper content of the liver of healthy animals was about twenty-five times greater than that for affected animals.

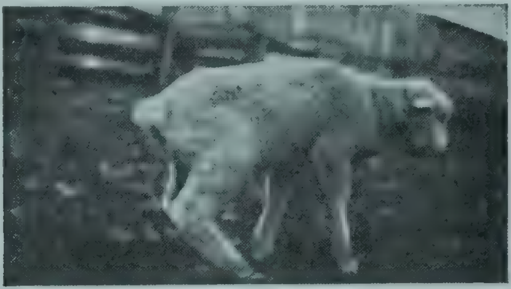


FIG. 35. Ataxic lamb due to a deficiency of copper. (Courtesy of H. W. Bennetts)

In mature sheep the most noticeable manifestation of a copper deficiency is the loss of crimp from the wool, which becomes stringy in appearance. Other symptoms that may be observed are anemia, diarrhea, and unthriftiness. Ewes suffering from a deficiency of copper show hemosiderosis. This finding early afforded evidence that the condition was not due to a lack of iron.

The minimum amount of copper required by the sheep has not been determined, but 5 mg. of copper per day has proved adequate for ewes in western Australia[36] in areas where the pastures are extremely deficient in copper. The addition of 0.25 to 0.5 per cent of copper sulfate ($CuSO_4 \cdot 5H_2O$) to salt would furnish about 10 mg. of copper per day.

Cobalt. The conclusion that cobalt is essential for sheep was the outcome of work on a wasting disease of unknown etiology occurring in localized sections in Western Australia, South Australia, and New Zealand. More recently it has been found that a deficiency of cobalt occurs in areas of Scotland, Kenya, Michigan, Wisconsin, Florida, Massachusetts, New Hampshire, and Alberta. Sheep grazed on these affected areas lost their appetite, wasted, and finally died of starvation, although surrounded by a luxuriant growth of pasture. The disease due to a cobalt deficiency has been referred to by a number of local names as bush sickness in New Zealand, pine in Scotland, nakuruitis in Kenya, coast disease in South Australia, lake shore disease in Michigan, salt sick in Florida, and enzootic marasmus in Western Australia. The latter name most adequately characterizes the disease. Figure 36 shows an animal with typical symptoms.

Originally the malady was believed to be due to a deficiency of iron. Aston[1] had shown that the administration of relatively large amounts of certain crude iron compounds including limonite was effective in curing or preventing the onset of the disease. As experience with the disease became wider it became apparent that limonites derived from different districts were not equally effective and that some samples gave negative results.

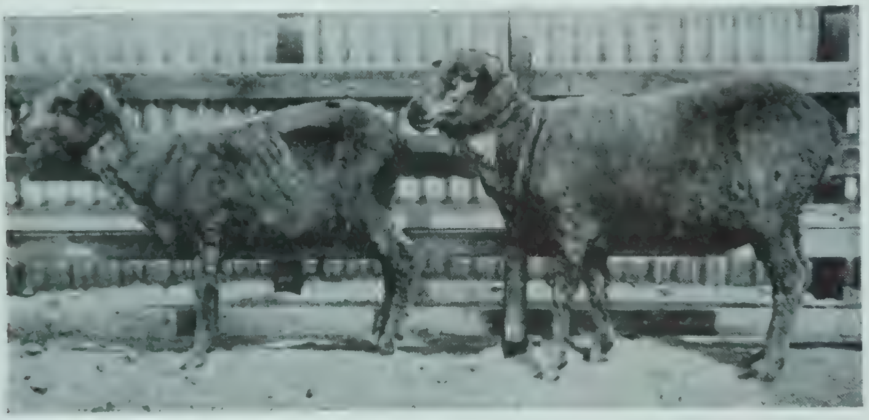


FIG. 36. Ewe on left pastured on cobalt-deficient area. Ewe on right received supplement of cobalt and pastured on same area. (Reproduced from Austral. Council Sci. Ind. Res. Bull. 113, 1938. Courtesy of H. R. Marston.)

The discovery by Underwood[63] that the livers and spleens of affected sheep contained excessive amounts of iron made it apparent that the response obtained by Aston from feeding crude iron compounds was due to some trace element present in the limonites. Further experiments[12] demonstrated that an iron-free extract of limonite was as potent a cure of enzootic marasmus as the limonite itself. Subsequently these workers demonstrated conclusively that the beneficial properties of the effective limonites were due to small amounts of cobalt that were present.[65]

The recommended allowances of sheep for cobalt cover a wide range. Filmer and Underwood[13] suggest 0.1 mg. of cobalt daily for sheep, while other workers[6] have fed 0.75 mg. The ability of the animal to store cobalt is apparent from the work of Corner and Smith[8] who found that the feeding of 1 mg. of cobalt daily for fourteen days was sufficient to take care of the requirements for six months when sheep were confined to land on which a cobalt deficiency normally developed. From the data available it appears that 0.1 mg. of cobalt daily is sufficient to meet the needs of ewes. Adequate amounts of cobalt may be provided in deficient areas by feeding salt containing 2.8 g. of cobalt chloride or cobalt sulfate per 100 pounds.

Underwood and Harvey[66] found that soils from areas endemic to enzootic marasmus contained 0.6 microgram of cobalt per gram whereas healthy soils contained 10 micrograms of cobalt per gram. The cobalt content of the pastures on the affected areas averaged 0.04 microgram per gram of dry forage as compared to 0.18 microgram for forage grown in healthy areas. The application of small amounts of cobalt fertilizer in the order of 54 g. of cobalt per acre as the acetate was effective in increasing to normal levels the cobalt content of the herbage.

Salt. Sodium, potassium, and chlorine are all known to be dietary essentials. Potassium occurs in plants in amounts that insure an adequate amount in rations made up of natural feedstuffs. In contrast, the amounts of sodium and chlorine present in feeds and especially in those of plant origin tend to be rather low.

Although the common salts of sodium and potassium are freely soluble, insuring complete absorption from the intestine, nature has made no provision for storing these elements in an insoluble and inactive form. Sodium chloride normally passes through the animal in rather large amounts. While sodium and potassium are much alike chemically and physically, they serve different biological roles as both plants and animals have universally accepted potassium as the main cellular base and sodium as the extracellular ion.

The excretion of sodium chloride by the renal pathway follows very closely the amount ingested. When the intake is low the amount of sodium and chlorine excreted falls to a very low level, the body seemingly conserving its meager supply for vital functions. The metabolism of sodium chloride appears to be closely associated with the adrenal glands. Following adrenalectomy the sodium and chloride contents of the serum falls to a very low level. Adrenalectomized animals have been kept alive for indefinite periods by the administration of extra amounts of salt, whereas signs of adrenal insufficiency promptly develop when the ingestion of salt is discontinued.

A deficiency of sodium chloride results in excessive fatigue, decreased feed consumption, and a decreased efficiency in the utilization of feed nutrients. The latter effect may be due to adverse effects on the action of the digestive enzymes. Sheep that are deprived of adequate salt develop a craving and may resort to chewing wood, licking dirt, and other manifestations of an unsatisfied diet. When salt is fed *ad libitum*, it is probable that sheep consume somewhat more than is needed to meet their minimum requirements. In a series of dry-lot tests Briggs[7] found that lambs having free access to salt consume an average of about 9 g. daily and that larger sheep eat slightly more. This is appreciably higher than the minimum level found by Terroine and Reichert[58] to give maximum rate of gain. They found that sheep made the most rapid growth and showed maximum nitrogen retention when the ration provided not less than 0.1 g. of salt per kilogram of body weight per day.

Excessive intakes of sodium chloride are injurious. The practice of mixing salt with concentrates for the purpose of reducing the intake of the concentrates when self fed is not to be recommended.

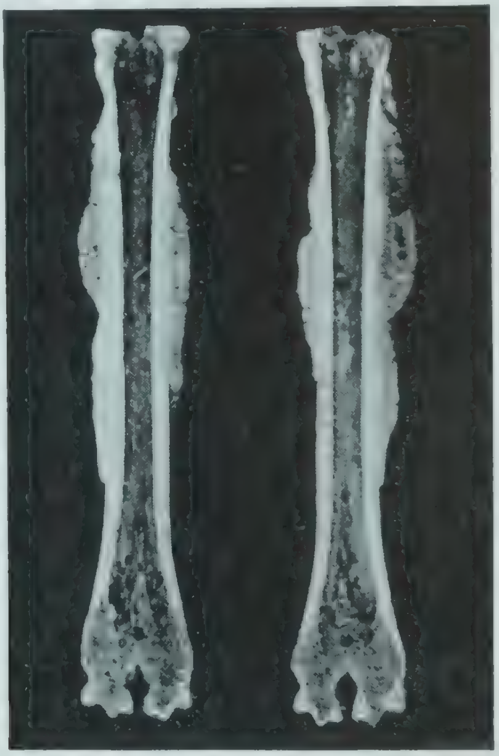


Fig. 37. Longitudinal section of metatarsus of sheep showing diffuse deposits and thickening due to fluorine toxicity. (Reproduced from Arch. für Tierheilkunde **67**: 420, 1934. Courtesy of Kaj Rohlm.)

Fluorine Toxicity. In certain parts of the world fluorine may occur in the drinking water or in feed components in amounts sufficient to exert deleterious effects on the animal. In certain parts of North Africa, India Japan, China, and Iceland, chronic fluorosis is reported to be endemic. Early records call attention to a disease of sheep in Iceland which generally appeared after periodic volcanic eruptions. Following the eruption of Hekla, many sheep died of acute fluorine toxicity within a few weeks, although the most serious trouble occurred several months later when symptoms of emaciation, weakness and impairment of the use of the limbs, thickening of the joints and development of exostosis of the long bones and jaws became apparent, as shown in Figure 37.

The major danger from fluorine is the use of rock phosphates that contain fluorine in amounts sufficient to be toxic. Rock phosphate generally contains from 3 to 4 per cent of fluorine.[26] In the manufacture of superphosphates, varying quantities, depending on the method, of the fluorine may be driven off by volatilization. Fluorine appears to exert an accumulative effect as the symptoms may not be manifest until the second or even third year on low levels of fluorine intake.

The toxicity of fluorine for sheep and the symptoms have been reported in some detail by Peirce.[49] The animals generally exhibit anorexia of varying degrees. The normal ivory color of the bones gradually changes to a chalky white; there is an increase in the thickness of the bones and exostosis of the long bones. The teeth, particularly the incisors, become pitted and eroded sometimes to such an extent that the nerves are exposed.

According to Mitchell [40] incipient symptoms of fluorosis may appear in sheep when the ration on a dry basis contains 0.012 per cent of fluorine. He proposes that permissible levels of fluorine for sheep be set at 0.003 per cent of the total dry ration. This level of fluorine would be approximately equivalent to feeding a mineral mixture containing 0.20 per cent of fluorine.

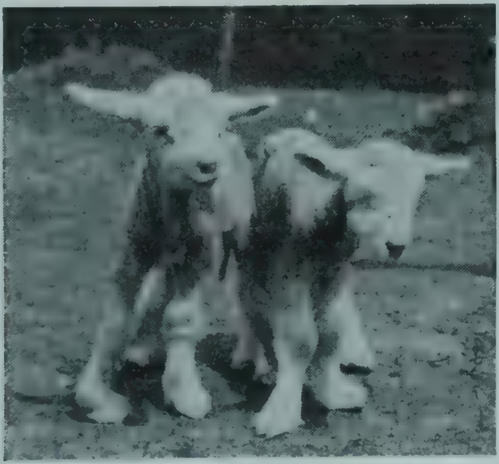


FIG. 38. Lambs showing congenital deformities induced by prenatal feeding on seleniferous forage. (Courtesy of the Wyoming Agr. Expt. Sta.)

Selenium Toxicity. A condition often referred to as "alkali disease" has been known for many years as a chronic condition in livestock in certain regions of the Great Plains of the United States. The symptoms may appear after the animals have been on affected areas for only a few weeks. The most common manifestations of selenium toxicity in sheep are dullness, emaciation, soreness and sloughing of the hoofs and stiffness of the joints, as shown in Figure 38. The terminal stage is characterized by almost complete blindness and varying degrees of paralysis. Atrophy and cirrhosis of the liver and atrophy of the heart are common post-mortem findings.

According to Moxon[44] chronic selenium toxicity occurs when animals consume feed containing from 5 to 40 micrograms of selenium per gram on a dry basis. The extent to which plants take up selenium varies greatly. Some species of plants are known to contain as much as 1000 micrograms on seleniferous soils while other species grown on the same soil may contain not more than 10 or 25 micrograms per gram.

A finding of considerable interest and possible application is the fact that small amounts of arsenic are effective in counteracting the toxicity for selenium.[9, 43] Arsenic added to drinking water at the rate of 5 p.p.m. or 10 p.p.m. to the feed was effective in protecting rats from selenium toxicity and similar results have been obtained with farm animals.

Molybdenum Excess. In Somerset, England, and in California, a scouring disease referred to as "teartness" occurs in cattle and sheep. The malady is most prevelant during seasons of the year when there is fast growth of the herbage. According to Ferguson and co-workers[11] animals start to scour within a few days after being turned on the teart pastures. The feces of sheep become very soft, the fleeces become stained, and the animals rapidly lose condition. The condition was shown to be due to the presence of molybdenum at levels of 20 to 100 micrograms per gram of dry herbage. The scouring could be prevented by the feeding of 2 g. of copper sulfate daily to cows. Smaller amounts of copper sulfate would be expected to be effective in controlling the condition in sheep.

Other Nutritional Disturbances

Pregnancy disease, also referred to as acetonemia, ketonemia, and domsiekte, an ailment of ewes in late pregnancy, has been reported from practically every part of the world where sheep are kept. It is much more common in ewes carrying twins or triplets than in ewes carrying single lambs.

Among the first symptoms are a loss of appetite and a staggering gait. Vision is frequently impaired, and the ewe will frequently stagger in circles and then fall. In the final stages she frequently exhibits partial paralysis and may pass into a state of coma. If parturition occurs during the earlier stages of the disease recovery usually results. The two most characteristic clinical features of the disease are a marked ketosis and extreme fatty infiltration of the liver. In ketonemic pregnant ewes the glycogen content of the liver is reduced to negligible amounts.[57] This reduction in liver glycogen appears to be associated with fatty infiltration of the liver.

The total acetone bodies in the blood of normal ewes average 3.0 mg. per 100 ml. of blood, whereas ewes with pregnancy disease were found to have values of up to 38 mg. per 100 ml.[18] The total acetone bodies excreted by affected ewes per 24 hours may run as high as 2000 mg. as compared to 25 mg. for normal healthy ewes. Hypoglycemia is a significant feature of the disease, the blood glucose level falling as low as 25 mg. per 100 ml. in some cases. It appears that the hypoglycemia is not the direct cause of the disease but that it is only one of the manifestations of a fundamental metabolic disturbance. The blood glucose level of sheep has been reduced to 10 mg. per 100 ml. by the injection of insulin without any apparent ill effects.[24] Apparently the sheep can withstand very low blood glucose levels.

Symptoms of pregnancy disease have been produced experimentally by feeding pregnant ewes rations of poor quality or rations low in energy.[15, 18] On the other hand, Shaw and Daugherty [56] fed pregnant ewes on a diet low in protein or one where the energy intake was limited to 50 per cent of the requirements. The only symptom characteristic of pregnancy disease that they observed was a milk hypoglycemia. It is apparent from the data in the literature that the etiology of pregnancy disease remains to be elucidated.

Urinary calculi may cause considerable loss especially among lambs in the feed lot. The incidence of urinary calculi in sheep in various sections of Colorado has been described in some detail by Newsom.[45] Although the etiology of urinary calculi is not entirely known, it appears that more than one factor may be responsible for the development of urolithiasis. The feeding of rations containing an excess of magnesium [28] or rations high in calcium, magnesium, and phosphorus [4] to lambs did not result in urolithiasis. Evidence that urinary calculi may be caused by an imbalance of minerals in the ration is afforded by the extensive studies of Polak [51] on laboratory animals. From the work of Schmidt [54] there is evidence that a deficiency of vitamin A may lead to urolithiasis.

Gastroenteritis, apoplexy, overeating disease, and food intoxication are names that have been applied to a malady of rather obscure etiology which is the cause of considerable loss in nursing and fattening lambs. The condition occurs among lambs that are fed a heavy allowance of grain. Recovery from the disease is rare, and the lambs usually die within a short time.[62] Affected lambs may throw back their heads, stagger, move in circles, or push against a fence, and then fall or die in convulsions. The disease may be prevented or kept to a minimum by preventing lambs from gorging on grain and by feeding roughage and grain in the proper proportions. Should the condition develop in the feed lot the grain should be omitted from the ration or the allowance reduced for a few feedings.

PRACTICAL CONSIDERATIONS

Sheep and goats are surpassed by no other domestic animal in their ability to utilize pastures. They are naturally adapted to grazing on pastures that supply a variety of forage plants. The feeding of cured hays and grains to breeding sheep and suckling lambs is not practiced extensively when there is an abundance of succulent grazing forage. Under conditions of scarcity due to overgrazing or unfavorable climatic conditions it is necessary to supplement the natural forage with other feeds. Under these conditions protein is likely to be one of the first limiting factors. Generally there is an insufficiency of energy, and frequently the phosphorus intake is low.

To provide nutrients for the development of the fetus especially during the last six weeks of gestation and for lactation supplementary feeding is essential in many localities. Depending on the amount of forage that is available a daily allowance of from one-eighth to one-half pound of a concentrate mixture may be necessary to meet the nutrient requirements. After lambing the allowance may be somewhat higher unless green grass is available. Ewes that are in good condition at the time of lambing may decrease slightly in weight during the first six weeks of lactation.

The use of supplements such as cottonseed, linseed, or soybean cake is very popular due to the convenience of feeding them and their high protein and phosophorus contents. Where protein supplements are relatively high in price some saving can be effected by using a concentrate consisting of equal amounts of a protein supplement, and corn, oats, barley, milo, or other cereal grains. The feeding of alfalfa or other good quality hays during periods when there is a shortage of natural forage also provides a source of carotene. The kind and amount of supplement for sheep and goats will depend on the availability of natural vegetation and should, therefore, be adapted to the different local conditions.

There is little need for the special preparation of feed for sheep and goats. They masticate their food very thoroughly and, except for young lambs and old ewes, there is generally no advantage to grinding corn, oats, barley, milo, or other grains. In fact there may be some disadvantage where the grain is ground very fine due to decreased palatability or digestive disturbances. Sometimes the amount of feed consumed can be increased by chopping the hay and mixing it with the concentrates.

The practice of providing extra feed for ewes just prior to and during the breeding season so that they will gain weight is referred to as flushing. It is believed that this increases the number of twin lambs. It is doubtful if this practice has any value for ewes that are already in good condition. On the other hand, it is to be expected that ewes that are thin may benefit from a general improvement in nutritional status by the extra allowance of feed.

BIBLIOGRAPHY

1. Aston, B. C., *N. Z. J. Agr.* **28**: 301, 381; **29**: 14, 84 (1924); **44**: 171, 367 (1932).
2. Auchinachie, D. W., and Fraser, A. H. H., *J. Agr. Sci.* **22**: 560 (1932).
3. Bechdel, S. I., Hilston, N. W., Guerrant, N. B., and Dutcher, R. A., *Pa. Agr. Expt. Sta. Bull.* **364** (1938).
4. Beeson, W. M., Pence, J. W., and Holm, G. C., *Am. J. Vet. Res.* **4**: 120 (1943).
5. Bennetts, H. W., and Beck, A. B., *Austral. Council Sci. Indust. Research Bull.* **147** (1942).
6. Bowstead, J. E., Sackville, J. P., and Sinclair, R. D., *Sci. Agr.* **22**: 479 (1942).
7. Briggs, H. M., Unpublished data (1944).
8. Corner, H. H., and Smith, A. M., *Biochem. J.* **32**: 1800 (1938).
9. Du Bois, K. P., Moxon, A. L., and Olson, O. E., *J. Nutrition* **19**: 477 (1940).
10. Duckworth, J., Godden, W., and Thomson, W., *J. Agr. Sci.* **33**: 190 (1943).
11. Ferguson, W. S., Lewis, A. H., and Watson, S. J., *J. Agr. Sci.* **33**: 44 (1943).
12. Filmer, J. F., and Underwood, E. J., *Austral. Vet. J.* **10**: 83 (1934).
13. Filmer, J. F., and Underwood, E. J., *Austral. Vet. J.* **13**: 57 (1937).
14. Fraser, A. H. H., Godden, W., and Thomson, W., *Veter. J.* **89**: 408 (1933).
15. Fraser, A. H. H., Godden, W., Snook, L. C., and Thomson, W., *J. Physiol.* **94**: 346 (1938).
16. Goettsch, M., and Papenheimer, A. M., *J. Exper. Med.* **54**: 145 (1931).
17. Griem, W. B., Hart, E. B., Kalkus, J. W., and Welch, H., *Nat'l. Res. Council, Reprint and Circ. Ser.* **111** (1942).
18. Groenewald, J. W., Graf, H., Bekker, P. M., Malan, J. R., and Clark, R., *Onderstepoort J. Vet. Sci. Animal Ind.* **17**: 245 (1941).
19. Guilbert, H. R., Miller, R. F., and Hughes, E. H., *J. Nutrition* **13**: 543 (1937).
20. Hamilton, T. S., Robinson, W. B., and Johnson, B. C., *J. Animal Sci.* **7**: 26 (1948).
21. Hammond, J., "Farm Animals, Their Breeding, Growth and Inheritance." London, Edward Arnold & Co. (1940).
22. Harris, L. E., and Mitchell, H. H., *J. Nutrition* **22**: 167, 183 (1941).
23. Hickman, K. C. D., and Harris, P. L., *Advances Enzymol.* **6**: 469 (1946).
24. Hitchcock, M. W. S., and Phillipson, A. T., *J. Physiol.* **105**: 42 (1947).
25. Innes, J. R. M., and Shearer, G. D., *J. Compar. Path. Therap.* **53**: 1 (1940).
26. Jacob, K. D., and Reynolds, D. S., *J. Assoc. Official Agr. Chem.* **11**: 237 (1928).
27. Johnson, B. C., Wiese, A. C., Mitchell, H. H., and Nevins, W. B., *J. Biol. Chem.* **167**: 729 (1947).
28. Johnson, D. W., Palmer, L. S., and Nelson, J. W., *Vet. Med.* **35**: 353 (1940).
29. Jones, J. M., and Stangel, W. L., *Texas Agr. Expt. Sta. Bull.* **563** (1938).
30. Loosli, J. K., and Harris, L. E., *J. Animal Sci.* **4**: 435 (1945).
31. Lundsgaard, E., *Bull. Johns Hopkins Hosp.* **63**: 1 (1938).
32. Madsen, L. L., McCay, C. M., and Maynard, L. A., *Cornell Agr. Expt. Sta. Mem.* **178** (1935).
33. Marston, H. R., *Austral. Council Sci. Ind. Research Bull.* **61** (1932).
34. Marston, H. R., *Austral. J. Expt. Biol. Med. Sci.* **9**: 235 (1932).
35. Marston, H. R., *Rept. 4th Intern. Grasslands Congress. Aberystwyth, G. B. Plen. Sec.* p. 26 (1937).
36. Marston, H. R., and McDonald, I. W., *Austral. Council Sci. Indust. Research Bull.* **113** (1938).
37. Marston, H. R., and Robertson, T. B., *Austral. Council Sci. Ind. Research Bull.* **39** (1928).
38. Maynard, L. A., *J. Nutrition* **32**: 345 (1946).

39. McElroy, L. W., and Goss, H., *J. Nutrition* **20**: 527, 541 (1940); **21**: 163, 405 (1941).
40. Mitchell, H. H., *Nat'l. Research Council Reprint Circ. Ser.* No. **113** (1942).
41. Mitchell, H. H., *J. Animal Sci.* **6**: 365 (1947).
42. Morris, S., and Ray, S. C., *Biochem. J.* **33**: 1209 (1939).
43. Moxon, A. L., and Rhian, M., *Physiol. Rev.* **23**: 305 (1943).
44. Moxon, A. L., *S. Dakota Agr. Expt. Sta. Bull.* **311** (1937).
45. Newsom, I. E., *J. Am. Vet. Med. Assoc.* **92**: 495 (1938).
46. Pearson, P. B., Briggs, H. M., Kammlade, W. G., Miller, J. I., and Miller, R. F., *Nat'l. Research Council Rept.* Recommended nutrient allowances for domestic animals. V. (rev.) (1949).
47. Pearson, P. B., and Darnell, A. L., *J. Nutrition* **31**: 51 (1946).
48. Peirce, A. W., *Austral. Council Sci. Ind. Research Bull.* **84** (1934).
49. Peirce, A. W., *Austral. Council Sci. Ind. Research Bull.* **121** (1938); *Nutrition Abst. Rev.* **9**: 253 (1939).
50. Peirce, A. W., *Austral. J. Expt. Biol. Med. Sci.* **23**: 295 (1945).
51. Polak, A., "Experimental formation of kidney and bladder stones by dietary means." Med. Dissertation, Bigot en Van Rossum, N. V., Amsterdam, 67 pp. (1936). Nederl. Tijschr. v. Geneek. **83**: 4009 (1939).
52. Rittenberg, D., and Shemin, D., *Ann. Rev. Biochem.* **15**: 247 (1946).
53. Sarett, H. P., and Goldsmith, G. A., *J. Biol. Chem.* **167**: 293 (1947).
54. Schmidt, H., *Am. J. Vet. Res.* **2**: 373 (1941).
55. Schweigert, B. S., Pearson, P. B., and Wilkening, M. C., *Arch. Biochem.* **12**: 139 (1947).
56. Shaw, J. C., and Daugherty, F. C., *J. Animal Sci.* **5**: 180 (1946).
57. Snook, L. C., *J. Physiol.* **97**: 238 (1939).
58. Terroine, E. F., and Reichert, T., *Compt. rend. Acad. Sci.* **190**: 768 (1930).
59. Thomas, B. H., and Cannon, C. Y., *Proc. Am. Soc. Animal Prod. 30th Annual Meeting,* p. 59 (1937).
60. Thomas, B. H., La Grange, W. F., and Culbertson, C. C., *J. Animal Sci.* **1**: 61 (1943).
61. Thomas, J. W., Loosli, J. K., and William, J. P., *J. Animal Sci.* **6**: 141 (1947).
62. Thorp, F., Jr., *Mich. Agr. Expt. Sta. Quart. Bull.* **23**: 186 (1941).
63. Underwood, E. J., *Austral. Vet. J.* **10**: 87 (1934).
64. Underwood, E. J., and Curnow, D. H., *Austral. Vet. J.* **20**: 282 (1944).
65. Underwood, E. J., and Filmer, J. F., *Austral. Vet. J.* **11**: 84 (1935).
66. Underwood, E. J., and Harvey, R. J., *Austral. Vet. J.* **14**: 183 (1938).
67. Verges, J. B., *Proc. 4th International Congress of Animal Breeding, Zurich,* p. 317 (1939).
68 Wiese, A. C., Johnson, B. C., Mitchell, H. H., and Nevens, W. B., *J. Nutrition* **33**: 263 (1947).
69. Willman, J. P., Loosli, J. K., Asdell, S. A., Morrison, F. B., and Olafson, P., *J. Animal Sci.* **4**: 128 (1945).
70. Willman, J. P., Morrison, F. B., and Klostesman, E. W., *Cornell Univ. Mimeo. Rept.* (1944).
71. Winegar, A. H., Pearson, P. B., and Schmidt, H., *Science* **91**: 508 (1940).
72. Woodman, H. E., *Biol. Revs.* **5**: 273 (1930).

Chapter XVII

THE NUTRITION OF POULTRY

HARRY W. TITUS

Limestone Products Corporation of America, Newton, New Jersey

Poultry includes all domesticated birds, such as chickens, ducks, geese, guineas, ostriches, peafowl, pigeons, swans, and turkeys. The word may be used also in referring to those gallinaceous upland game birds that have been reproduced for several generations in captivity; these include pheasants, quail, partridges, and grouse. By many persons, however, the words *poultry* and *chickens* are used interchangeably, and the other kinds of poultry are referred to by their specific names.

The nutrition of the chicken has been studied more intensively than that of any other kind of poultry—probably more intensively than that of any other animal. In any case, it may be said, without fear of successful contradiction, that more is known about the quantitative nutrient requirements of the chicken than of any other animal, even including man. Since 1930 some quantitative information has been obtained about the nutrient requirements of the turkey. Very much less is known about the nutrition of the duck, the pigeon, the goose, and the other kinds of poultry. Successful methods of feeding all the other kinds of poultry are known, however.

Differences Between Poultry and Other Animals. From the standpoint of nutrition, there are some marked differences between poultry and most other animals, particularly mammals. In discusing those differences the chicken may be considered as largely representative of all poultry.

In mammals the nutrition of the embryo and of the nursling is dependent to a considerable extent on the contemporary nutrition of the mother. In the chicken the nutrition of the embryo is fixed as soon as the shell is formed on the egg. However, the nutrition of the mother, during the development of the ovum and the subsequent formation of the egg, determines the composition of the egg and the nutrition of the embryo in the egg. Also, the temperature and humidity of the environment in which the egg is incubated have certain effects on the development of the embryo. After hatching, the nutrition of the chick is dependent for a time, but only in part, on the yolk; it is almost entirely dependent on the feed the chick consumes. The nutrition of the newly hatched young of the pigeon, however, is dependent to a considerable extent on the contemporary nutrition of the parents.

The alimentary canal of the chicken is comparatively short. It consists of the mouth, first section of the gullet (esophagus), crop, second section of the gullet, proventriculus (glandular stomach), gizzard, small intestine, large intestine (rectum), cloaca, and anus. Two ceca are attached at the junction of the small and large intestines. The chicken has no teeth; all grinding of feed is done by the gizzard, with or without the aid of grit.

In the chicken, urine is not stored in a bladder; it is passed directly from the kidneys through the ureters to the cloaca, where it is mixed with the fecal masses from the large intestine. The urine and the feces are excreted together, and this circumstance makes it more difficult to determine digestibility of feed in the chicken than in the mammal.

The protein metabolism of the chicken differs significantly from that of the mammal. The end-product of protein metabolism in the chicken is largely uric acid (2,6,8-trioxypurine; $C_5H_4N_4O_3$), whereas in most mammals it is largely urea (carbamide; NH_2CONH_2). As a result of this difference, there are other differences; [8] these are shown in Table 102.

TABLE 102. COMPARISON OF PROTEIN METABOLISM IN THE MAMMAL AND THE BIRD *

Class	Heat Production per Gram kg.-cals.	O_2 Consumption per Gram cc.	CO_2 Production per Gram cc.	H_2O Production per Gram g.	Respiratory Quotient $\left(\frac{CO_2}{O_2}\right)$	CO_2 Thermal Quotient $\left(\frac{\text{Kg.-cals.}}{\text{G. of } CO_2}\right)$	O_2 Thermal Quotient $\left(\frac{\text{Kg.-cals.}}{\text{G. of } O_2}\right)$
Mammalia	4.316	966.3	733.9	0.3960	0.801	2.838	3.124
Aves	3.84	891.1	628.6	0.47	0.705	3.11	3.02

* Based on data given by Loewy [70] on the metabolism of protein and the data of Coulson and Hughes [29] on the composition of the urine of chickens.

Differences Among Poultry. The feed consumed by chickens and pigeons consists largely of concentrates. Chickens are truly omnivorous, whereas pigeons are granivorus. Pigeons normally eat almost no roughage, and most modern chickens eat very little. Turkeys, guineas, and ducks are good foragers and eat much more roughage than chickens. Geese are the best foragers of all and are able to subsist almost entirely on roughage.

The normal young of the chicken, turkey, and guinea store but little fat. Ducklings store more fat than chicks, squabs store as much or more fat than ducklings, and goslings store more than the young of the other kinds of poultry. Adult poultry of all kinds are able to store large quantities of fat, but the adult goose excels them all as a producer and storer of fat.

UTILIZATION OF FEED

The modern chicken is outstanding as a converter of plant and animal materials, not satisfactory as human food, into meat and eggs, which are very desirable and nutritious human foods. With certain strains of chickens it now is possible to produce a 4- to 5-pound bird in 14 weeks by the use of only 3.5 pounds of feed for each pound of live bird. Thus, to produce a bird that weighs 4.5 pounds, only 15.75 pounds of suitably formulated feed are required.

The high-production strains of chickens are, likewise, very effcient converters of feed into food. For example, a 4-pound White Leghorn pullet that lays 250 eggs in her first year of production will consume only about 78.5 pounds of feed while she is laying those eggs. Thus, in this instance, only about 3.8 pounds of feed are required for the production of a dozen eggs, or only 2.5 pounds of feed per pound of eggs.

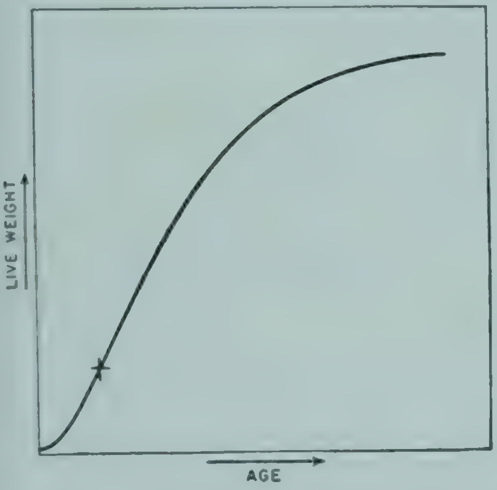


Fig. 39. The relationship between live weight and age in many animals. The cross marks the point of inflection of the growth curve: at this point the rate of growth is at its maximum. In the chicken the maximum rate of growth usually occurs just before one-half of the growth is completed. (From page 451, *Yearbook of Agriculture*, 1939.)

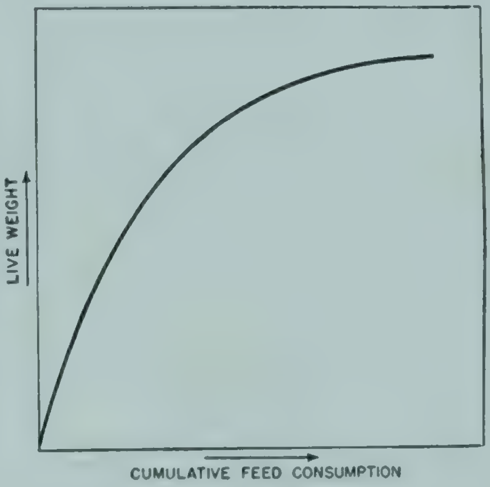


Fig. 40. The relationship between live weight and cumulative feed consumption in many animals, including the various kinds of poultry. (From page 451, *Yearbook of Agriculture*, 1939.)

The number of pullets that produce as many as 300 eggs during their first year of production has been increasing since 1930. Of these pullets, those that weigh about 4 pounds (e.g., White Leghorn pullets) require only about 3.32 pounds of feed per dozen eggs, or only about 2.2 pounds of feed per pound of eggs.

It should not be assumed that poultry meat and eggs are regularly produced as economically as is indicated in the preceding three paragraphs. On the average: about 22 pounds of feed are required to produce a bird weighing 4.5 pounds, and about 6.4 pounds of feed to produce a dozen eggs.

The possibility, however, of producing poultry meat and eggs much more economically than they are now being produced is clearly indicated.

Growth (Meat Production). The growth of a chicken usually is measured by the increase in its live weight. If the live weights of a chicken at different ages are plotted against those ages, a growth curve similar to the one in Figure 39 is obtained; but if the same live weights are plotted against the quantities of feed required to attain them, the resulting curve is like that in Figure 40.

If, in a similar manner, the efficiency of feed utilization—the ratio of the gain in live weight to the weight of feed required to produce the gain—is plotted against age and against live weight, respectively, curves similar to those in Figures 41 and 42 are obtained. Efficiency of feed utilization is a linear function of live weight, that is, it decreases in direct proportion to the live weight.

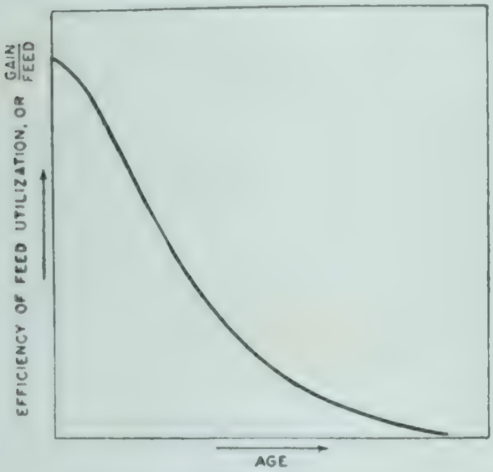


Fig. 41. How the efficiency of feed utilization decreases as the age of the chicken increases. (From page 452, *Yearbook of Agriculture*, 1939.)

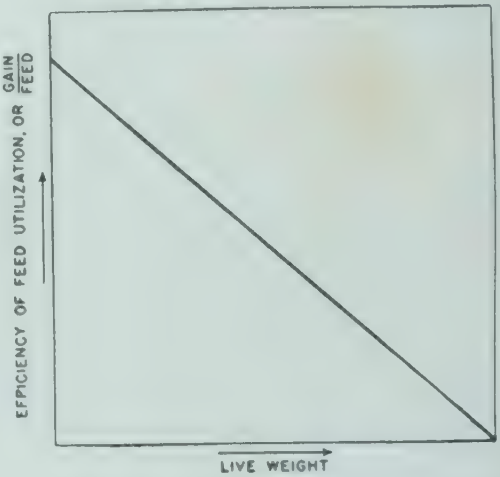


Fig. 42. How the efficiency of feed utilization decreases as the live weight of the chicken increases. (From page 452, *Yearbook of Agriculture*, 1939.)

The relationship between the live weight and the feed consumption of chickens,[106] on an adequate diet of fixed composition, follows a simple, definite law, known as the law of diminishing returns. The way in which this law operates is shown in Figure 43, in which the average live weight of a group of chickens was plotted against their average cumulative feed consumption.

The figures beneath the curve in Figure 43 are the gains in live weight resulting from the consumption of each successive 2 kg. of feed. In this particular instance, the second 2 kg. of feed produced only 78.62 per cent as much gain as the first 2 kg., the third 2 kg. produced only 78.62 per cent as much gain as the second 2 kg., and so on. As a result of the operation of the law of diminishing returns, the eighth 2 kg. of feed produced less than one-fifth as much gain as the first 2 kg.

If, in Figure 43, the gains were shown for each kilogram of feed, instead of for each 2 kg., it would be found that the second kilogram produced only 88.67 per cent as much gain as did the first, the third kilogram only 88.67 per cent as much gain as did the second, and so on.

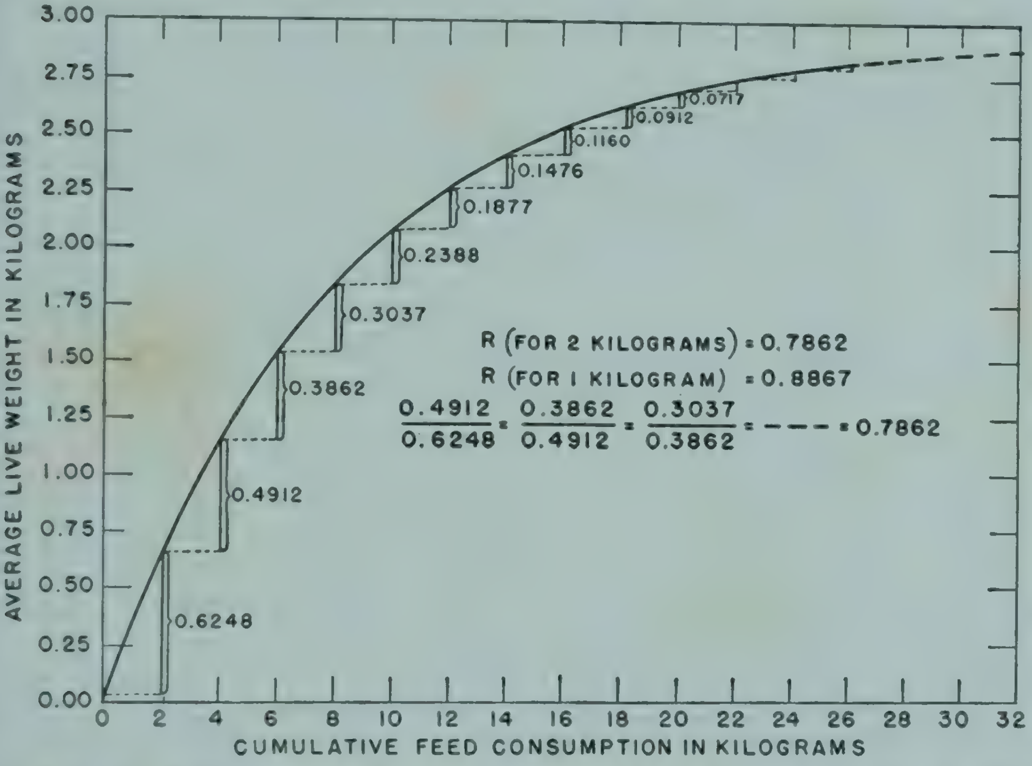


FIG. 43. Illustrative of how the law of diminishing returns operates in feeding chicks. The equation of the curve is $w = A - BR^f$, in which w is the live weight for any cumulative feed consumption, f. A is the maximum live weight attainable as a result of growth; $(A-B)$ is the initial live weight; B is the total gain in weight possible as a result of growth; R is the inverse ratio of the gains of live weight resulting from the consumption of any two successive equal weights of feed; and f is the cumulative feed consumption. In the curve shown, if the "successive equal weights of feed" are 1 kilogram, the value of R is 0.8867; if the "successive equal weights of feed" are 2 kilograms, the value of R is 0.7862.

Level of Feed Intake. An interesting phenomenon in many growing animals, including chickens and other poultry, is that the efficiency of feed utilization is less at full feed than it is at any level of feed intake between about 50 per cent and full feed. The effect of the level of feed intake on the efficiency of feed utilization is shown in Table 103.

The data in Table 103 indicate that the maximum gain per unit weight of feed consumed is made when the level of feed intake is between 50 and 60 per cent of full feed. Other data indicate that the maximum efficiency of feed utilization is sometimes observed when the level of feed intake is between 60 and 70 per cent of full feed. In any case, the maximum efficiency of utilization of feed for growth is obtained when the level of feed intake is appreciably less than full feed.

In the practical production of poultry meat it is difficult, if not impossible, to take advantage of this phenomenon. There are several reasons: first, chickens grow more slowly on levels of feed intake less than full feed than they do when the feed intake is maximum; second, the maximum live weight is appreciably less on the lower levels of feed intake than it is on the higher levels; and, third, the quality of the final product (the dressed carcass) is very much poorer at the lower levels of feed intake than it is at the higher levels. According to the data in Table 103, it would take more than twice as much time, with the same brooding and housing facilities, to produce the same live weight of chickens at the 50 per cent level of feed intake as it would at the full-feed level. By feeding 69 per cent more feed at the full-feed level than at the 50 per cent level, one would obtain nearly 57 per cent more live weight in about 27 per cent less time. Moreover, the chickens produced on the 50 per cent level of feed intake would have a very much lower market value than those produced on the full-feed level.

TABLE 103. EFFECT, IN MALE CHICKENS OF THE HEAVIER BREEDS, OF THE LEVEL OF FEED INTAKE ON THE RELATIVE EFFICIENCY OF UTILIZATION OF FEED FOR GROWTH, THE RELATIVE MAXIMUM LIVE WEIGHT ATTAINED, THE RELATIVE QUANTITY OF FEED REQUIRED FOR ATTAINING THE MAXIMUM LIVE WEIGHT, AND THE RELATIVE LENGTH OF TIME REQUIRED TO ATTAIN MAXIMUM LIVE WEIGHT ON A DIET CONTAINING ABOUT 19.4 PER CENT OF CRUDE PROTEIN *

Level of Feed Intake as Per Cent of Full Feed	Relative Average Efficiency of Utilization of Feed for Growth %	Relative Maximum Live Weight[1] Attained %	Relative Quantity of Feed Required for Attaining Maximum Live Weight[1] %	Relative Length of Time Required to Attain Maximum Live Weight[1] %
20	90.7	19.1	21.1	105.1
30	93.3	51.1	54.7	103.6
40	97.2	77.7	79.9	101.9
50	100.0	100.0	100.0	100.0
60	99.1	114.9	116.0	98.1
70	96.8	127.7	131.9	94.9
80	94.8	138.3	145.9	89.9
90	93.1	148.9	159.9	82.0
100	92.6	156.6	169.2	73.2

* From page *809, Yearbook of Agriculture,* 1939.

[1] This refers to the maximum live weight that is eventually attained after a prolonged period of feeding at the levels indicated in the first column.

Feed Required by Different Kinds of Poultry. The different kinds of poultry, and the different breeds of chickens as well, are not equally efficient in their utilization of feed for growth. The available data indicate that ducks and turkeys are more efficient than the heavier breeds of chickens, and these, in turn, are more efficient than the lighter breeds of chickens. A few comparative data on the feed required by different kinds of poultry to attain certain selected average live weights are given in Table 104. No two of the diets that were fed in obtaining these data were the same, and, for that reason, these data do not provide an exact comparison of the different kinds of poultry in utilizing feed for growth. Nevertheless, diets suitable for each kind of poultry were fed, and hence the data indicate in a general way the relative efficiencies with which chickens, turkeys, and ducks utilize feed for growth.

TABLE 104. QUANTITIES OF FEED REQUIRED TO OBTAIN CERTAIN SELECTED AVERAGE LIVE WEIGHTS WITH DIFFERENT KINDS OF POULTRY

	Kind of Poultry and Quantity of Feed Required per Bird					
Average Live Weight lb.	White Leghorns [Males and Females][1] lb.	White Leghorns [Males] lb.	Crossbreds[2] [Males] lb.	Rhode Island Reds [Males] lb.	Turkeys[3] [Males] lb.	White Pekin Ducks [Males[1] and Females] lb.
0.5	1.38	1.30	1.29	1.12	0.95	0.83
1.0	3.18	3.00	2.91	2.53	2.20	2.01
1.5	5.27	4.94	4.65	4.05	3.49	3.28
2.0	7.75	7.21	6.52	5.69	4.83	4.66
2.5	10.80	9.93	8.56	7.49	6.21	6.17
3.0	14.75	13.34	10.78	9.46	7.65	7.83
3.5	20.39	17.91	13.24	11.66	9.15	9.68
4.0	. . . .	24.84	15.97	14.13	10.70	11.77
4.5	. . . .	39.75	19.07	16.95	12.32	14.17
5.0	. . . .	. . . .	22.62	20.25	14.02	16.99

[1] For a group containing approximately the same number of birds of each sex.

[2] The male offspring resulting from mating Barred Plymouth Rock females with Rhode Island Red males.

[3] Several different breeds from parent stock which had been selected for small size.

The efficiency of feed utilization for growth varies not only with the kind of poultry but with the adequacy of the diet consumed and the environmental conditions as well. It now is possible to formulate diets that are used somewhat more efficiently for growth than those that were fed in obtaining the data in Table 104.

Per Cent of Protein in the Diet. From the standpoint of animal nutrition, growth is essentially a storage of protein.[50] It is true, of course, that other substances are stored simultaneously, and that water is stored in even greater quantity than is protein; nevertheless, the growth of an animal is peculiarly characterized by the increase in the protein content of its body. It is logical to conclude, therefore, that the per cent of protein in the diet of the chicken affects its growth. The experience of many poultrymen, as well as of research workers in poultry nutrition,[47] have shown this conclusion to be correct.

The effect of the per cent of protein in the diet of male chickens on their relative efficiency in utilizing feed for growth, as well as on their maximum live weight and the length of time required to attain it, is shown in Table 105. According to the data in Table 105, the optimum per cent of protein in the diet is about 21 per cent. As the per cent of protein is decreased or increased from approximately 21, the efficiency of the utilization of feed for growth decreases. The data in Table 105 do not hold for all possible diets, nor are they exact for all breeds of poultry, or all strains within any one breed, on any fixed diet; they show in a general way, however, the effect of different percentages of protein in the diet on growth and the efficiency of the utilization of feed for growth.

TABLE 105. EFFECT, IN THE MALE CHICKEN, OF THE LEVEL OF PROTEIN INTAKE ON THE RELATIVE EFFICIENCY OF THE UTILIZATION OF FEED FOR GROWTH, THE RELATIVE MAXIMUM LIVE WEIGHT ATTAINED, THE RELATIVE QUANTITY OF FEED REQUIRED FOR ATTAINING THE MAXIMUM LIVE WEIGHT, AND THE RELATIVE LENGTH OF TIME REQUIRED TO ATTAIN THE MAXIMUM LIVE WEIGHTS *

Relative Level of Protein Intake as Per Cent of Total Feed Consumed	Relative Average Efficiency of the Utilization of Feed for Growth %	Relative Maximum Live Weight[1] Attained %	Relative Quantity of Feed Required for attaining Maximum Live Weight[1] %	Relative Length of Time Required to Attain Maximum Live Weight[1] %	Relative Level of Protein Intake as Per Cent of Total Feed Consumed	Relative Average Efficiency of the Utilization of Feed for Growth %	Relative Maximum Live Weight[1] Attained %	Relative Quantity of Feed Required for attaining Maximum Live Weight[1] %	Relative Length of Time Required to Attain Maximum Live Weight[1] %
13.	67.7	97.6	144.1	119.9	20.	99.7	99.8	100.1	100.5
14.	80.6	97.9	121.3	111.7	21.	100.0	100.0	100.0	100.0
15.	87.3	98.2	112.5	107.8	22.	97.9	100.2	102.3	99.7
16.	91.5	98.6	107.7	104.6	23.	94.3	100.4	106.4	99.5
17.	94.6	98.9	104.6	102.6	24.	90.2	100.5	111.4	99.4
18.	97.2	99.2	102.1	101.5	25.	85.6	100.6	117.5	99.2
19.	98.7	99.5	100.7	101.0					

* From page *813*, *Yearbook of Agriculture*, 1939.

[1] This refers to the maximum live weight that is attained when the birds are fully grown.

Whether, in a given diet, 21 per cent of protein is the optimum quantity depends on the content of the several amino acids in the protein. If all the amino acids are present in such proportion that there is little or no wastage of any of them, the optimum quantity of protein may be appreciably less than 21 per cent. On the other hand, if several of the amino acids are present in such proportion that there is considerable wastage of some of them, the optimum quantity of protein may be appreciably greater than 21 per cent. If, however, the per cent of protein is very much more than 23 per cent, there is the distinct possibility of additional wastage resulting from the utilization of protein for purposes other than the building of tissues.

Even though the optimum per cent of protein in the diet is about 21 per cent, it may be more economical to use a diet that contains only 18 or 19 per cent of protein. In most cases the difference in cost between a diet containing 21 per cent of protein and one containing only 18 or 19 per cent will be an important factor in determining the most economical per cent of protein in the diet, but both the relative efficiencies and the costs of the diets should be considered.

Hormones and Fat Deposition. Since 1938, a number of studies [38, 61, 71, 72, 73, 99, 102] have been made of the effect of estrogens and certain chemical compounds—for example, thiouracil—on fat metabolism in both growing and adult chickens. The immediate effect of the administration of estrogens, either by injection, implantation, or feeding, is an increase in the content of fat and calcium in the blood. The ultimate result is an increased deposition of fat not only in and under the skin but even in the muscle tissues.

In the male chicken, the continued administration of estrogens causes marked changes in its appearance (feminization). The comb shrivels, loses its turgor, and droops; and the feathers take on the appearance of those of a female rather than of those of a male. The effects on the comb may be prevented by the administration of androgens [62] (for example, by feeding cow manure dried at a temperature below 45° C. or by rubbing a small quantity of methyl testosterone into the comb). The effective use of estrogens on male chickens is sometimes referred to as hormonal or chemical caponizing. The rate of growth, as measured by gain in weight, usually is not affected by hormonal caponizing; however, the character of the gains is changed, in that they contain more fat.

In using estrogens in finishing (fattening) chickens for market the two most outstanding effects are: (1) the fat content of the muscle tissues is increased greatly, and (2) the dark meat becomes lighter in color and more tender.

The inclusion of thiouracil in the feed of growing chickens, at a level of 0.2 per cent, has been reported to stimulate the deposition of fat and to improve the market grade of the carcasses.[38, 66] Unless it can be demonstrated conclusively that none of the thiouracil is retained in the edible tissues of the chickens, it should not be used in treating birds intended for human consumption.

Egg Production. In the egg-laying chicken, feed is used primarily for two purposes: maintenance and the formation of eggs. In the pullet, which normally begins to lay before its growth is completed, some feed is used for growth, especially up to the age of approximately 40 weeks. In the hen some feed is used for regaining weight that was lost during the molt.

Several investigators have attempted to partition the feed consumed by laying chickens into that used for maintenance and that used for the formation of eggs. According to the studies of the writer[103] and of Brody, Funk, and Kempster,[24] approximately 0.9 pound of feed, in addition to that used for maintenance, is required for the production of one egg. Byerly,[25] however, concluded that about 0.14 pound of feed is required. In either case, it follows that of two chickens of equal live weight, the one that lays the larger number of eggs requires the more feed. Moreover, of these two chickens, the one that lays the most eggs requires less total feed per egg and, hence, is a more economical producer of eggs.

TABLE 106. ESTIMATES OF THE TOTAL FEED REQUIRED BY CHICKENS OF DIFFERENT LIVE WEIGHTS FOR MAINTENANCE AND THE PRODUCTION OF 0, 100, 150, 200, 250, AND 300 EGGS, RESPECTIVELY, PER YEAR

Average Live Weight lb.	Average Total Feed Required per Chicken per Year for Maintenance and the Production of the Indicated Number of Eggs					
	0 Eggs lb.	100 Eggs lb.	150 Eggs lb.	200 Eggs lb.	250 Eggs lb.	300 Eggs lb.
2.0	34.1	43.0	47.4	51.9	56.3	60.7
2.5	40.0	48.9	53.3	57.7	62.2	66.6
3.0	45.7	54.5	59.0	63.4	67.9	72.3
3.5	51.1	60.0	64.4	68.9	73.3	77.7
4.0	56.3	65.2	69.7	74.1	78.5	83.0
4.5	61.4	70.3	74.7	79.2	83.6	88.0
5.0	66.3	75.2	79.6	84.1	88.5	92.9
5.5	71.1	80.0	84.4	88.8	93.3	97.9
6.0	75.7	84.6	89.1	93.5	97.9	102.4
6.5	80.3	89.2	93.6	98.1	102.5	106.9
7.0	84.8	93.6	98.1	102.5	107.0	111.4

In studies of the maintenance requirement of chickens, the writer[103] found that about 0.14 pound of feed is required per day for the maintenance of a 3.5-pound chicken. On the basis that the quantity of feed required, above maintenance, to produce one egg is 0.0888 pound, and that the maintenance requirement is proportional to the 0.73 power of the live weight, estimates have been made of the total quantity of feed required, per year, to produce certain selected numbers of eggs. These estimates are given in Table 106.

According to the estimates in Table 106, the quantity of feed required to maintain a chicken one year increases about 10 pounds (9.1 to 11.6 pounds) for each increase of 1 pound in the chicken's live weight. Thus, a 5.5 pound chicken requires about 10 pounds more feed for maintenance than a 4.5 pound chicken.

In order to illustrate the relation between the quantity of feed consumed per dozen eggs and the average annual production, Figure 44 is presented. In this figure, curves for three different groups of White Leghorn pullets show that such pullets, if they lay only 100 eggs per year, will require between 7.7 and 8.7 pounds of feed per dozen eggs; but if they lay as many as 200 eggs per year, they will require only 4.4 to 4.9 pounds of feed per dozen eggs.

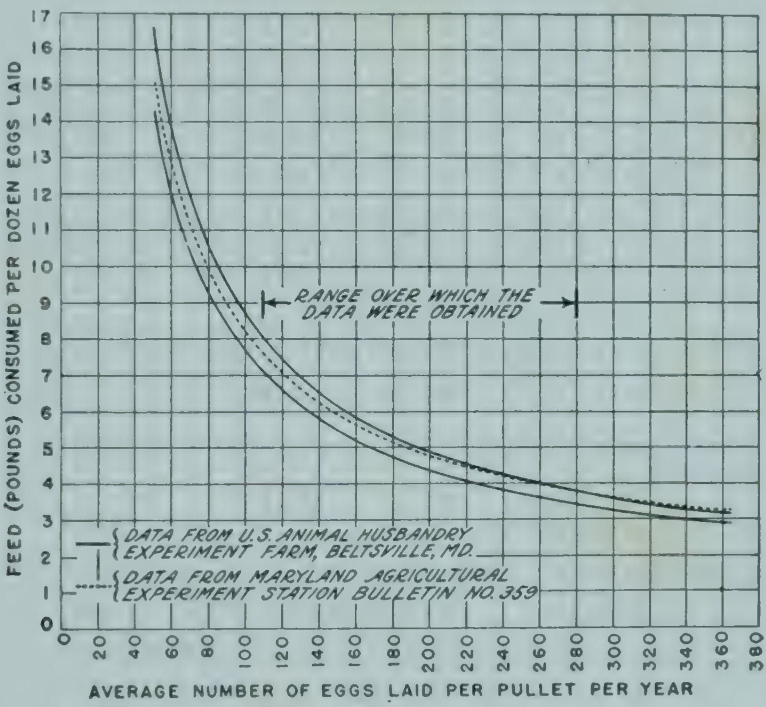


FIG. 44. The relationship between the quantity of feed consumed per dozen eggs and the average number of eggs laid per pullet per year. (Data obtained in different years from two different lots of White Leghorn pullets at the Beltsville Res. Center, Beltsville, Md. and from Md. Agr. Expt. Sta. Bull. 359, 1934.)

The efficiency of egg production—the number of eggs laid per pound of feed consumed—as a function of the average annual egg production is illustrated in Figure 45. This figure shows that chickens of the heavier breeds lay fewer eggs per pound of feed than chickens of the lighter breeds. In general, the efficiency tends to decrease as the live weight increases. Of course, it is known that different strains of the same breed often differ greatly in weight and that even strains that have the same average weight may be somewhat different in their ability to utilize feed for egg production. Accordingly, the curves in Figure 45 do not hold precisely for all White Leghorn and Rhode Island Red pullets and hens, but only for those that were used in obtaining the data from which the curves were drawn.

Level of Feed Intake. In feeding chickens for the production of eggs, it is important to maintain the maximum consumption of feed at all times. A simple example will show why. If a 3.5-pound chicken is to produce at the rate of an egg per day for any extended period of time and not lose weight, she must consume each day about 0.14 pound of feed for maintenance and about 0.09 pound of feed for making the egg, or a total of about 0.23 pound of feed. If, for any reason, the total feed consumption is reduced 10 per cent, or to 0.207 pound, the portion available for the production of eggs is reduced more than 25 per cent.

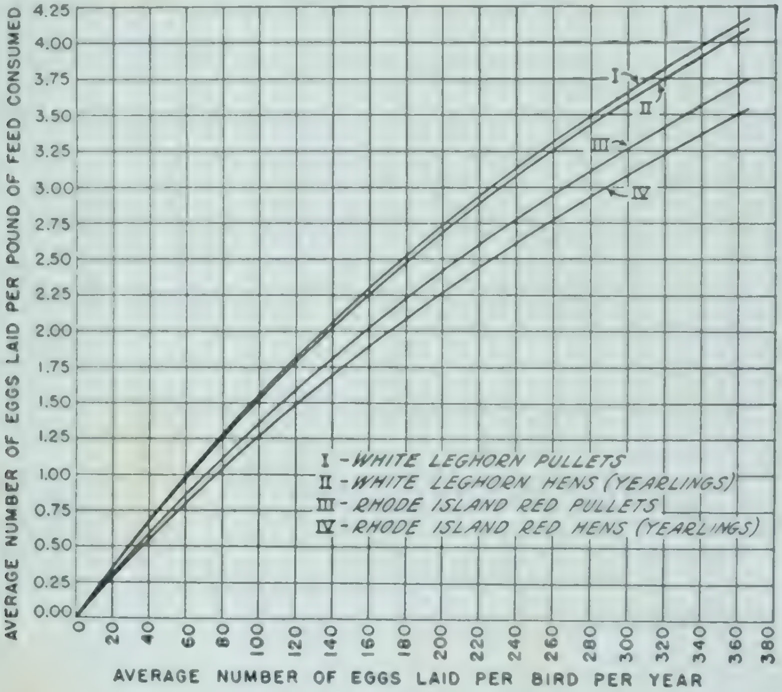


FIG. 45. The relationship between the number of eggs laid per pound of feed consumed and the average number of eggs laid per chicken per year. (Data from Beltsville Res. Center, Beltsville, Md.)

In a study of the effect of reducing feed consumption on egg production, Heywang[58] found that when he reduced the feed consumption of a flock of White Leghorn chickens 12.5 per cent, the egg production was reduced about 32.5 per cent. When the feed consumption was reduced 25 per cent, the egg production was reduced about 53.7 per cent. In general, the higher the level of egg production is, the more it is affected when the feed consumption is reduced any given per cent.

Per Cent of Protein in the Diet. There is slightly more than 7 g. of protein in an average 2-ounce egg. This protein is of very high biological value. When a typical diet is fed to laying chickens, the quantity consumed each day must contain from 10.5 to 12.5 g. of digestible protein, in order to yield, for the production of an egg, about 7 g. of protein of the required composition. Usually this quantity of digestible protein can be obtained, by the chicken, from 12.5 to 15 g. of crude protein. Accordingly, the feed of a typical White Leghorn pullet that is laying at the rate of 200 eggs per year should contain between 13.5 and 16 per cent of protein, and that of a typical Rhode Island Red pullet that is to lay the same number of eggs should contain between 11.5 and 13.5 per cent.

In general, the feed of laying chickens should contain 14 to 16 per cent of crude protein. The lower level is satisfactory for chickens of the heavier breeds, and the higher level, for chickens of the lighter breeds. Feeds intended for both breeds should contain about 15 to 16 per cent of crude protein. The required quantity of protein, in any given case, will depend on its amino acid content; that is, on how nearly the percentage distribution of the amino acids in the digestible protein of the feed approximates that of the amino acids in an egg.

If the feed contains less than the required quantity of protein—actually the required quantity of the several amino acids—egg production will be decreased correspondingly. If, however, the feed contains more of the required amino acids than is needed, the excess will be wasted—at least so far as egg production is concerned.

Effect of Diet on Quality of Poultry Meat and Eggs

Poultry Meat. Both the proximate composition and flavor of poultry meat are influenced by the feed that is consumed. When the several cereal grains are used singly in the finishing (fattening) feed, the site of deposition of the fat depends on which grain is used. Corn, for example, causes a high per cent of the deposited fat to be in the flesh and a much smaller per cent to be in the abdominal cavity and skin, whereas barley, oats, and wheat have the opposite effect in varying degree.[75, 88]

It has been claimed that the fat of oats-fed birds is superior in flavor to that of corn-fed birds.[63] The flesh of chickens (especially the females) that have received estrogens, for example, diethylstilbestrol and the dimethyl ether of diethylstilbestrol, has been reported to be more "highly flavored" than the flesh of chickens to which no estrogen has been fed.[38]

The inclusion of some fish oils and some fish meals in the diet of turkeys tends to produce a fishy flavor, especially in the skin.[5, 74] Some lots of fish meal produce a much more pronounced fishy flavor than others. The flesh of chickens also may acquire a fishy flavor if cod-liver oil is included in the feed.[27] If the oil is omitted from the feed two weeks or more before the chickens are killed, there is little or no fishy flavor in the flesh. In turkeys, however, the fishy flavor may persist 11 weeks or more after fish products have been omitted from the feed.

The feeding of a finishing diet to chickens in fattening batteries usually causes the deposition of large quantities of fat.[51, 63] The inclusion of beef fat, mutton fat, corn oil, or other digestible oil in the finishing feed increases fat deposition.[43]

White-fleshed chickens may be produced by the use of white grains, such as oats,[44] in the finishing diet. The effect of the white grains may be enhanced by including skim milk [44] or buttermilk in the feed. On the other hand, yellow-colored flesh and skin (in the yellow-skin breeds) may be produced by including large quantities of yellow corn, corn gluten meal, and alfalfa meal in the feed. Fish oils rich in vitamin A suppress the deposition of yellow pigments in the skin.[46]

In general, the age and sex of individual birds determines the percentage of fat in their carcasses. Young birds contain much less fat than adult birds, and adult females tend to contain more fat than adult males. For example, when turkeys are about 16 weeks old, the total edible portion usually contains less than 4.5 per cent of fat, but by the time they are 32 weeks old the fat content may have increased to about 21 per cent in the males and to about 28 per cent or more in the females.[52]

Eggs. The diet has only a slight effect on the proximate composition of the edible portion of the eggs of the several kinds of poultry. The diet, however, may affect the quality of the eggshells (strength and texture), the color of the yolks, the physical and chemical characteristics of the fat in the yolks, and the vitamin content of both the whites and the yolks. Moreover diet has a very marked effect on hatchability.

An adequate supply of calcium, manganese, iodine, and vitamin D is necessary for the production of eggs with sound shells, and for good hatchability as well.

The color of the yolks of eggs is influenced by the quantity of xanthophyll in the feed. Diets containing large quantities of fresh green feed, alfalfa meal, corn, and corn gluten meal usually cause the yolks to have a more pronounced color. The use in the diet of fish oils rich in vitamin A tends to reduce the quantity of pigment deposited in the yolks. The kind of fat in the egg yolks depends to a considerable extent on the kind of fat in the feed. The vitamin content of eggs is dependent on the vitamin content of the feed. It is comparatively easy to increase the content of vitamin A, vitamin D, thiamine, riboflavin, and pantothenic acid of eggs by increasing the quantities of these vitamins in the feed.

The inclusion of large quantities of cottonseed meal in the diet usually has an undesirable effect on the color of the yolks of the eggs that are produced. If there is as much as 30 per cent of cottonseed meal in the total feed, the yolks of many of the eggs will have a dark color and mottled appearance when laid. If such eggs are stored, the yolks often acquire a dark brown color after a week or two. Even when the total feed contains as little as only 6 to 10 per cent of cottonseed meal, the yolks of the eggs may become dark colored if held in stroage for 6 weeks or longer. Cottonseed meal from which the pigment glands have been removed does not have this effect.[40]

Often the feed is blamed when an undesirable flavor is observed in eggs. It has been claimed that certain materials, for example, onions, rape, turnips, and some fish meals, when fed in large quantities, have an undesirable effect on the flavor of eggs. Nevertheless, when undesirable flavors are found in eggs, a few eggs from each chicken in the flock should be examined, because an occasional bird produces eggs that have an objectionable odor or flavor. If individual birds that produce such eggs are found, they should be removed from the flock. More often than not an undesirable flavor in an egg is not caused by the feed. Eggs very easily and quickly acquire undesirable flavors if they come in contact with onions, garlic, fish oil, or certain disinfectants.

NUTRIENT ALLOWANCES FOR POULTRY

When, in 1944, the Subcommittee on Poultry Nutrition[100] of the National Research Council prepared their report on Recommended Nutrient Allowances for Poultry, they found it desirable to distinguish between "allowances" and "requirements." Such a distinction was desirable because, for many years, students of animal nutrition had used the latter term to designate the minimum quantities of nutrients required to promote normal growth and reproduction. As thus used, "requirements" made no allowances for margins of safety to provide for (1) variations in the composition of feedstuffs, (2) variations in the feed requirements of different strains and breeds of the same species, (3) the losses of nutrients in the manufacture, transportation, and storage of formula feeds, and (4) variations in the use of formula feeds. The Subcommittee used "allowance" as a term that includes both the actual requirement and a suitable margin of safety. The margin of safety was not the same for all nutrients; it was determined, as it were, by the composite experience of the Subcommittee. In the pages that follow, the terms "allowance" and "requirement" are used in essentially the same sense as used by the Subcommittee.

National Research Council's Recommended Nutrient Allowances for Chickens. On November 1, 1946, and in March, 1950, the Subcommittee revised its recommended nutrient allowances for poultry. The revised nutrient allowances for chickens are given in Tables 107 and 108.

It is extremely difficult to make, from commonly used feedstuffs, a diet for chicks that contains 0.9 per cent of lysine, 0.5 per cent of methionine, 0.4 per cent of cystine, and 0.25 per cent of tryptophan, and at the same

TABLE 107. NATIONAL RESEARCH COUNCIL'S RECOMMENDED NUTRIENT ALLOWANCES FOR CHICKENS (REVISED MARCH, 1950)

Nutrient	Chicks [0-8 wks.]	Chicks [8-18 wks.]	Laying Hens	Breeding Hens
Total protein, %	20	16	15	15
Calcium, %	1	1	2.25[1]	2.25[1]
Phosphorus, %[2]	0.6	0.6	0.75	0.75
Added salt [NaCl], %	0.5	.0.5	0.5	0.5
Manganese, mg. per lb.	25	?	?	15
[Manganese, p.p.m.]	[55]	[?]	[?]	[33]
Iodine, mg. per lb.[3]	0.5	0.3	0.3	0.5
[Iodine, p.p.m.]	[1.1]	[0.7]	[0.7]	[1.1]
Potassium, %	0.2	0.16	?	?
Vitamin A activity, I.U. per lb.[4]	2,000	2,000	3,300	3,300
Vitamin D, A.O.A.C. cu. per lb.	180	180	450	450
Riboflavin, mg. per lb.	1.6	0.9	0.9	1.3
Pantothenic acid, mg. per lb.	5	5	2.5	5
Choline, mg. per lb.	700	?	?	?
Niacin, mg. per lb.	8	?	?	?
Thiamine, mg. per lb.	0.9	?	?	?
Pyridoxine, mg. per lb.	1.6	?	1.6	1.6
Biotin, mg. per lb.	0.045	?	?	0.07

[1] Calcium supplements fed free choice may replace part of dietary calcium.

[2] Inorganic phosphorus should constitute 0.4% of the total feed.

[3] Allowance slightly larger than recommended by NRC in Rept. and Circ. Series No. 111, because of differences in feed supply.

[4] May be fish oil vitamin A or provitamin from vegetable sources.

See also notes and references in Table 108.

time only 20 per cent of protein. To supply these quantities of these particular amino acids, the *protein* in the feedstuffs would have to contain on the average 4.5 per cent of lysine, 2.5 per cent of methionine, 2.0 per cent of cystine, and 1.25 per cent of tryptophan. The protein of very few of our commonly used feedstuffs contains as much of these amino acids as the quantities just stated. To supply the quantities of the several amino acids tentatively recommended by the National Research Council it is

TABLE 108. NATIONAL RESEARCH COUNCIL'S RECOMMENDED AND TENTATIVE REQUIREMENTS FOR CHICKS (0–4 WEEKS) FOR CERTAIN AMINO ACIDS, VITAMINS, AND MINERALS (REVISED MARCH, 1950)

Recommended	
Amino acids:	
Glycine, %	1.0-1.5
Arginine, %	1.2
Methionine, %	0.9
or Methionine, %	0.5
and Cystine, %	0.4
Lysine, %	0.9
Tryptophan, %	0.25
Histidine, %	0.3
Leucine, %	1.4
Phenylalanine, %	1.6
or Phenylalanine, %	0.9
and Tyrosine, %	0.7
Threonine, %	0.6
Valine, %	0.8
Isoleucine, %	0.6
Tentative	
Vitamins:	
Vitamin K, mg. per lb.	0.18
Folic acid, mg. per lb.	0.35
Minerals:	
Magnesium, mg. per lb.	180
Iron, mg. per lb.	9.0
Copper, mg. per lb.	0.9

Notes applicable to Tables 107 and 108

[a] New standards of Vitamin D potency adopted in 1950: 100 old units [AOAC] equal 75 new units [I.U. chick].

[b] Choline and betaine interchangeable to some extent.

[c] References pertaining to Tables 107 and 108—

Protein, [98, 104]

Ca and P, [12, 32, 77, 87, 98, 104, 108, 109]
Mn, [38, 43, 98, 104]; I, [110]; K, [11, 37a]; Mg,

Vitamin A, [2, 10, 14, 76, 90, 91, 93, 94, 96, 97, 102, 104, 112]
Vitamin D, [89, 104]
Riboflavin, [13, 30, 87, 98, 104]
Pantothenic acid, [9, 37, 85, 107]
Choline, [65, 90]
Niacin, [21, 22, 98]
Thiamine, [8, 85]
Pyridoxine, [23, 90, 98]
Biotin, [55, 65]

Glycine, [65]; Arginine, [65, 67]; Methionine and Cystine, [illegible];
Lysine, [4, 66]; Tryptophan, [3, 98]

necessary, when ordinary feedstuffs are used, that the diet contain about 23 per cent of protein, or more.

Also, it may be pointed out that it is not possible to compound, from our commonly used feedstuffs, a diet for chicks that contains 1.1 p.p.m. of iodine (0.5 mg. per pound), unless a special source of iodine is added. A typical diet for chicks that does not contain a special source of iodine usually will contain not more than 0.3 p.p.m. of that element. Standard iodized salt cannot serve as that special source of iodine because it contains only 70 p.p.m. of iodine, and 0.5 per cent of it will add only 0.35 p.p.m. of iodine to the diet.

TABLE 109. SUMMARY OF NUTRIENT ALLOWANCES FOR GROWING CHICKENS (0–8 WKS.)

Nutrient	Desired Level	Practical Range
Protein [N x 6.25], %[1]	21.0	20.0-23.0, or more
Arginine, %	1.0	
Lysine, %	1.0	
Methionine, %	0.5	
Cystine, %	0.3	
Tryptophan, %	0.2	
Glycine, %	0.8	
Isoleucine, %	0.6	
Leucine, %	1.4	
Phenylalanine, %	0.95	
Threonine, %	0.7	
Valine, %	0.8	
Histidine, %	0.35	
Tyrosine, %	0.75	[replaceable by phenylalanine]
Calcium [total], %	1.2	1.0-1.5
Phosphorus [total], %	0.8	0.6-0.9
Inorganic phosphorus, %	0.2	0.2-0.3, or more
Salt [total], %	0.5	0.4-0.7
Added salt, %	0.3	0.25-0.4
Potassium, %	0.25	0.17-1.3
Magnesium, %	0.04	0.04-0.5
Manganese [total], p.p.m.	50	50-100, or more
Added manganese, p.p.m.	20	10-30, or more
Iodine [total], p.p.m.	5	2-5, or more
Added iodine, p.p.m.	4.5	2-4.5, or more
Iron, p.p.m.	30	30-100, or more
Copper, p.p.m.	3	3-5, or more
Cobalt, p.p.m.	?	0.05-0.2, or more
Vitamin A, I.U. per lb.	2,000	2,000-12,000, or more
Vitamin D, A.O.A.C. cu per lb.[2]	270	180-270, or more
Vitamin E, mg. per lb.	9	9-25, or more
Vitamin K, mg. per lb.	0.18	
Riboflavin, mg. per lb.[3]	1.7	1.6-1.8, or more
Pantothenic acid, mg. per lb.	5	5-7, or more
Choline, mg. per lb.	650	600-700, or more
Niacin, mg. per lb.[4]	7	7-50, or more
Thiamine, mg. per lb.	0.7	0.7-3.0, or more
Pyridoxine, mg. per lb.	1.5	
Biotin, mg. per lb.	0.045	
Folic acid, mg. per lb.	0.25	
Vitamin B_{12}, mg. per lb.	0.005	0.004-0.01

[1] Protein allowance may be reduced to 16% after 8th week: amino acid allowances may be reduced by 30%.

[2] See footnote (a) in Table 108.

[3] Riboflavin may be reduced after 8th week to 1.2 mg. per lb.

[4] Low tryptophan in diet demands more niacin and *vice versa*.

TABLE 110. SUMMARY OF NUTRIENT ALLOWANCES FOR LAYING AND BREEDING CHICKENS

Nutrient	Desired Level	Practical Range
Protein [N x 6.25], %	15.0	15.0-17.0
Arginine, %	0.50	
Lysine, %	0.45	
Methionine, %	0.37	
Cystine, %	0.19	
Tryptophan, %	0.12	
Glycine, %	0.18	
Isoleucine, %	0.61	
Leucine, %	0.70	
Phenylalanine, %	0.46	
Threonine, %	0.35	
Valine, %	0.56	
Histidine, %	0.17	
Tyrosine, %[1]	0.36	
Calcium [total], %	2.3	2.0-2.8 [see table 9a]
Phosphorus [total], %	0.8	0.7-1.3 [see table 9a]
Salt [total], %	0.5	0.4-0.7
Added salt, %	0.3	0.25-0.4, or more
Manganese, p.p.m.	50	35-100, or more
Added manganese, p.p.m.	20	10-30, or more
Iodine [total] p.p.m.	5	2-5, or more
Added iodine, p.p.m.	4.5	2-4.5, or more
Vitamin A, I.U. per lb.		
Laying chickens	3,300	3,300-12,000, or more
Breeding chickens	4,500	3,300-12,000, or more
Vitamin D , A.O.A.C. cu per lb.	500[2]	450-500, or more
Riboflavin, mg. per lb.		
Laying chickens	1.1	1.0-1.2, or more
Breeding chickens	1.5	1.4-1.6, or more
Pantothenic acid, mg. per lb.		
Laying chickens	4.5	4.0-4.5, or more
Breeding chickens	5.5	5.0-5.5, or more
Choline, mg. per lb.	500	450-500, or more
Pyridoxine, mg. per lb.	1.5	1.0-1.5, or more
Biotin, mg. per lb.	0.07	

[1] Replaceable phenylalanine.
[2] See note (a) Table 108.

TABLE 111. CORRESPONDING APPROXIMATE PERCENTAGES OF PHOSPHORUS AND CALCIUM[1] FOR ALL-MASH DIETS (TOTAL FEED) AND FOR LAYING MASHES WITH WHICH AN EQUAL QUANTITY OF GRAIN IS TO BE FED

All-mash Diets		Laying Mashes [with which Grain Is To Be Fed]		All-mash Diets		Laying Mashes [with which Grain Is To Be Fed]	
Phosphorus Content %	Calcium[2] Content %	Phosphorus Content %	Calcium[3] Content %	Phosphorus Content %	Calcium[2] Content %	Phosphorus Content %	Calcium[3] Content %
0.6	1.9	0.8	3.7	1.0	2.4	1.2	4.2
0.7	2.0	0.9	3.8	1.1	2.5	1.3	4.3
0.8	2.1	1.0	3.9	1.2	2.7	1.4	4.4
0.9	2.3	1.1	4.1	1.3	2.8	1.5	4.6

[1] Calcium supplements fed free choice are considered as a part of the diet.

[2] In all-mash diets the quantities of calcium may be only about 75% of those given if the chickens have free access to a calcium supplement.

[3] In laying mashes with which an approximately equal quantity of grain is to be fed the quantities of calcium may be only about 50% of those given if the chickens have free access to a calcium supplement.

Summary of Nutrient Allowances for Chickens. Elsewhere, the writer has discussed and summarized nutrient allowances for chickens.[105] His summary of nutrient allowances for growing chickens is given in Table 109, for laying and breeding chickens in Tables 110 and 111, and for other classes of chickens in Tables 112, 113, and 114.

TABLE 112. SUMMARY OF NUTRIENT ALLOWANCES FOR BROILERS BEING FINISHED (FATTENED) FOR MARKET

Nutrient	Desired Level or Practical Range
Protein [N x 6.25], %	16-20
Total fat [ether extract], %	4-8
Added fat, %	0-4
Vitamin D, A.O.A.C. cu per lb.[1]	180
Other vitamins	Approximately the same as for growing chickens
Mineral elements	Approximately the same as for growing chickens

[1] Should be derived from D-activated animal sterol rather than fish or fish-liver oils.

TABLE 113. SUMMARY OF NUTRIENT ALLOWANCES FOR FRYERS, ROASTERS, CAPONS, AND FOWLS BEING FINISHED (FATTENED) FOR MARKET

Nutrient	Desired Level or Practical Range
Protein [N x 6.25], %	12-14
Total fat [ether extract], %	6-10
Added fat, %	2.5-6, or more
Calcium, % about	1.0
Phosphorus, % about	0.5
Vitamin A, I.U. per lb.[1]	1,800, or more
Vitamin D, A.O.A.C. cu per lb.[2]	90

[1] Should be supplied by alfalfa meal or other plant source of vitamin A, rather than fish or fish-liver oils.

[2] Should be derived from D-activated animal sterol, rather than fish or fish-liver oils.

TABLE 114. SUMMARY OF NUTRIENT ALLOWANCES FOR SEGREGATED BREEDING MALES

Nutrient	Desired Level or Practical Range
Protein [N x 6.25], %	13-14, or more
Calcium, %	0.6-0.9
Phosphorus, %	0.4-0.6
Vitamin A, I.U. per lb.	2,000, or more
Vitamin D, A.O.A.C. cu per lb.	75, or more
Riboflavin, mg. per lb.	1, or more
Other vitamins	?
Other minerals	Approximately the same as for growing chickens

Nutrient Allowances for Turkeys. The turkey is very efficient in utilizing feed for growth. Only 4 to 5 pounds of feed are required per pound of live weight to raise and finish turkeys for market. Thus, on the average, to produce a 17.5-pound turkey, ready for market, only about 79 pounds of total feed are required. Cline[28] has tabulated the average weights, gains in weight, and feed consumption of turkeys (average of males and females) for each week to 28 weeks. Table 115 is a condensation of his tabulation.

TABLE 115. THE AVERAGE WEIGHT OF TURKEYS, GAINS IN WEIGHT, CUMULATIVE FEED CONSUMPTION, AND FEED REQUIRED PER POUND OF GAIN, BY MONTHS, TO THE AGE OF 7 MONTHS

Age Months	Average Weight[1] lb.	Gain per Month lb.	Total Feed Consumption		Feed Required per Lb. of Gain	
			Per month lb.	Cumulative lb.	Per month lb.	Cumulative lb.
0	0.12[2]	-	-	-	-	
1	0.85	0.73	1.02	1.02	1.40	1.40
2	2.51	1.66	3.57	4.59	2.15	1.92
3	5.01	2.50	7.48	12.07	2.99	2.47
4	8.27	3.26	11.60	23.67	3.56	2.90
5	12.01	3.74	14.82	38.49	3.96	3.24
6	15.19	3.18	18.00	56.49	5.66	3.75
7	17.09	1.90	20.40	76.89	10.74	4.53[3]

[1] Average of males and females.
[2] Initial live weight.
[3] Pounds of feed per pound of live bird: 4.50.

In general the growing turkey requires a higher content of protein and certain vitamins in its feed than does the chicken. The nutrient allowances recommended by the Subcommittee on Poultry Nutrition of the National Research Council[100] are given in Table 116.

The other nutrient requirements and allowances of turkeys are not well established. In any case, the requirements of the poult for arginine[69] and lysine[39] appear to be at least 30 per cent greater than those of the chick; and it is not unlikely that the requirements of the poult for the other amino acids are proportionately higher than those of the chick. According to Boucher,[17] the poult's requirement for certain of the vitamins are as follows: niacin, 23 mg. per pound; pantothenic acid, 5.3 mg. per pound; pyridoxine, 1.4 mg. per pound; biotin, 0.05 mg. per pound; and folic acid, about 0.5 to 0.75 mg. per pound.

Nutrient Allowances for Other Kinds of Poultry. The duck is comparable to the turkey in its efficiency in utilizing feed for growth. To produce a 6.5 pound duck only about 29 pounds of feed are required;

thus the average quantity of feed required per pound of live weight, to produce a 6.5 pound duck, is only about 4.46 pounds.

Very little is known about the actual nutrient requirements of the duck. Apparently it has a rather low requirement of vitamin A, and a requirement of vitamin D as great as or a little greater than that of the chicken. Increases in the average weight of experimental groups of ducks follow increases in the vitamin D allowances up to a level of at least 150 A.O.A.C. chick units per pound.[33, 78] A suitable allowance is between 180 and 270 A.O.A.C. chick units per pound.

TABLE 116. NATIONAL RESEARCH COUNCIL'S RECOMMENDED NUTRIENT ALLOWANCES FOR TURKEYS (REVISED MARCH, 1950) [1]

Nutrient	Poults [0–8 wks]	Poults [8–16 wks]	Breeding Turkeys
Total protein, %	28	20[2]	15
Calcium, %	2	2	2.25[3]
Phosphorus,[4] %	1	1	0.75
Added salt [NaCl], %	0.5	0.5	0.5
Manganese, mg. per lb.	25	?	15
Vitamin A activity, IU per lb.	4,000	4,000	4,000
Vitamin D, AOAC cu per lb.	800	800	800
Riboflavin, mg. per lb.	2	?	1.8
Pantothenic acid, mg. per lb.	6	?	?
Choline, mg. per lb.	900	?	?

[1] See also notes in Tables 107 and 108.

[2] From 16 weeks to market weight, protein may be reduced to 16%.

[3] Calcium supplements fed free choice may replace part of dietary calcium.

[4] Inorganic phosphorus should constitute 0.4% of total feed. References pertaining to Table 116 (at end of chapter)—Protein,[48, 82, 92]: Ca and P,[35, 49, 81, 104]: Mn,[104]: Vitamin A,[41, 59]: Vitamin D,[7, 15, 16, 45, 79, 111]: Riboflavin,[19, 20]: Choline,[31, 64].

Apparently, ducklings grow well on diets that contain 16 to 24 per cent of protein. A suitable allowance of protein is the same as that for the chick.

The riboflavin requirement of the duckling appears to be about the same as that of the chick [34] or, possibly, somewhat less. The niacin requirement of the duckling has been reported to be about 11 mg. per pound (2.5 mg. per 100 g.[54]), the pyridoxine requirement to be about 1.1 mg. per pound (0.25 mg. per 100 g.[53]), and the panthothenic acid requirement to be about 5.0 mg. per pound (1.1 mg. per 100 g.[60a]).

Almost nothing is known about the nutrient requirements of pigeons, peafowl, guineas, geese, and swans. Pigeons grow well and reproduce on a mixture of cereal grains and other seeds, if they have access to a mineral mixture that supplies supplementary calcium and salt. Diets suitable for either growing turkeys or growing chickens appear to be satisfactory for peafowl and guineas. Young geese and swans may be started on diets satisfactory for ducks; after a short time, they are able to forage for themselves.

Nutrient Allowances for Gallinaceous Upland Game Birds. The nutrient requirements of gallinaceous upland game birds are very similar to those of the turkey. There is evidence, however, that somewhat more protein is desirable, and as much or more vitamin D is required.

According to Norris et al.[86] and Callenbach and Hiller [26] a satisfactory level of protein intake for growing pheasants is 27 to 28 per cent. In studies of the nutrition of Bobwhite quail Nestler, Bailey, and McClure [85] found that a diet containing 28 per cent of protein gave the best results, but concluded that, after the birds are about two-thirds grown, a diet containing 22 per cent of protein is used as efficiently (in gaining weight) as one containing 28 per cent.

The requirements of game birds for calcium, phosphorus, manganese, and salt appear to be the same as those of turkeys. To prevent porosis in pheasants [98] and, presumably, in other game birds the diet must contain at least 35 p.p.m. of manganese.

As a result of studies in which more than 2000 Bobwhite quail were used, Nestler [83] concluded that the optimum levels of vitamin A are: for breeding stock, 6000 I.U. per pound of feed; for growing stock, 3000–4000 I.U., and for maintenance in winter 2500 I.U.

According to Boucher and Callenbach,[18] the vitamin D requirements of pheasants and quail are much higher than those of chickens. They found the vitamin D requirements of Bobwhite quail to be between 270 and 320 A.O.A.C. chick units per pound of feed and that of pheasants to be between 360 and 900 A.O.A.C. chick units per pound of feed.

The pheasant's requirement of riboflavin is reputed to be high, but the exact requirement is not known.

It is of more than passing interest that Nestler [84] has found the Bobwhite quail does not require grit.

BIBLIOGRAPHY

1. Almquist, H. J., *Proc. Expt. Biol. Med.* **49**: 544 (1942).
2. Almquist, H. J., and Mecchi, E., *Poul. Sci.* **18**: 129 (1939).
3. Almquist, H. J., and Mecchi, E., *Proc. Expt. Biol. Med.* **48**: 526 (1941).
4. Almquist, H. J., and Mecchi, E., *Proc. Expt. Biol. Med.* **49**: 174 (1942).
5. Anonymous, *U. S. Dept. Agr. Mimeo. A.H.D.* No. 74 (1944).
6. Arnold, A., and Elvehjem, C. A., *J. Nutrition* **15**: 403 (1938).
7. Baird, F. D., and Greene, D. J., *Poul. Sci.* **14**: 70 (1935).
8. Barott, H. G., Fritz, J. C., Pringle, E. M., and Titus, H. W., *J. Nutrition* **15**: 145 (1938).
9. Bauernfeind, J. C., Norris, L. C., and Heuser, G. F., *Poul. Sci.* **21**: 142 (1942).
10. Bearse, G. E., and Miller, W. M., *Poul. Sci.* **16**: 34, 39 (1937).
11. Ben-Dor, B., *Proc. Expt. Biol. Med.* **46**: 341 (1941).
12. Bethke, R. M., Kennard, D. C., Kick, C. H., and Zinzalian, G., *Poul. Sci.* **8**: 257 (1929).

13. Bethke, R. M., and Record, P. R., *Poul. Sci.* **21**: 147 (1942).
14. Biely, J., and Chalmers, W., *Can. J. Res. Sec. D, Zool. Sci.* **14**: 21 (1936).
15. Bird, H. R., *J. Nutrition* **27**: 377 (1944).
16. Boucher, R. V., *J. Nutrition* **27**: 403 (1944).
17. Boucher, R. V., *Absts. Cornell Nutr. Confer. Feed Mfgs.*, p. 54 (1946).
18. Boucher, R. V., and Callenbach, E. W., *Pa. Agr. Expt. Sta. Bull.* **480** (1946).
19. Boucher, R. V., Hill, F. W., Patrick, H., and Knandel, H. C., *Poul. Sci.* **20**: 456 (1941).
20. Boucher, R. V., Patrick, H., and Knandel, H. C., *Poul. Sci.* **21**: 466 (1942).
21. Briggs, G. M., Jr., Luckey, T. D., Tepley, L. J., Elvehjem, C. A., and Hart, E. B., *J. Biol. Chem.* **148**: 517 (1943).
22. Briggs, G. M., Jr., Mills, R. C., Elvehjem, C. A., and Hart, E. B., *Proc. Expt. Biol. Med.* **51**: 59 (1942).
23. Briggs, G. M., Jr., Mills, R. C., Hegsted, D. M., Elvehjem, C. A., and Hart, E. B., *Poul. Sci.* **21**: 379 (1942).
24. Brody, S., Funk, E. M., and Kempster, H. L., *Mo. Agr. Expt. Sta. Res. Bull.* **278** (1938); see also, Brody, S., "Bioenergetics and Growth," New York, Reinhold Publishing Corp. (1945).
25. Byerly, T. C., *Md. Agr. Expt. Sta. Bull.* **A1** (Tech.) (1941).
26. Callenbach, E. W., and Hiller, A. C., *Pa. Agr. Expt. Sta. Bull.* **299** (1933).
27. Carrick, C. W., and Hauge, S. M., *Poul. Sci.* **5**: 213 (1926).
28. Cline, L. E., *Nev. Agr. Exten. Serv. Bull.* **86** (1939).
29. Coulson, E. J., and Hughes, J. S., *Poul. Sci.* **10**: 53 (1930).
30. Davis, H. J., Norris, L. C., and Heuser, G. F., *Poul. Sci.* **17**: 81, 87 (1938).
31. Evans, R. J., *Poul. Sci.* **22**: 266 (1943).
32. Evans, R. J., Carver, J. S., and Brant, A. W., *Poul. Sci.* **23**: 9, 36 (1944).
33. Fritz, J. C., Archer, W., and Barker, D., *Poul. Sci.* **20**: 151 (1941).
34. Fritz, J. C., Archer, W., and Barker, D., *Poul. Sci.* **18**: 449 (1939).
35. Fritz, J. C., Hooper, J. C., and Moore, H. P., *Poul. Sci.* **24**: 324 (1945).
36. Gallup, W. D., and Norris, L. C., *Poul. Sci.* **18**: 76, 83 (1939).
37. Gillis, M. B., Heuser, G. F., and Norris, L. C., *Poul. Sci.* **21**: 470 (1942).
37a. Gillis, M. B., *J. Nutrition* **36**: 351 (1948).
38. Glazener, E. W., and Jull, M. A., *Poul. Sci.* **25**: 236 (1946).
39. Grau, C. R., Kratzer, F. H., and Asmundson, V. S., *Poul. Sci.* **25**: 529 (1946).
40. Groschke, A. C., Rubin, M., and Bird, H. R., *Poul. Sci.* **26**: 310 (1947).
41. Guilbert, H. R., and Hinshaw, W. R., *J. Nutrition* **8**: 45 (1934).
42. Gutowska, M. S., and Parkhurst, R. T., *Poul. Sci.* **21**: 277 (1942).
43. Gutteridge, H. S., and O'Neil, J. B., *Sci. Agr.* **21**: 350 (1941).
44. Gutteridge, H. S., and O'Neil, J. B., *Sci. Agr.* **21**: 607 (1941).
45. Hammond, J. C., *Poul. Sci.* **20**: 204 (1941).
46. Hammond, J. C., and Harshaw, H. M., *Poul. Sci.* **20**: 437 (1941).
47. Hammond, J. C., Hendricks, W. A., and Titus, H. W., *J. Agr. Research* **56**: 791 (1938).
48. Hammond, J. C., and Marsden, S. J., *Poul. Sci.* **18**: 11 (1939).
49. Hammond, J. C., McClure, H. E., and Kellogg, W. L., *Poul. Sci.* **23**: 239 (1944).
50. Hankins, O. G., and Titus, H. W., "Food and Life," Yearbook of Agriculture, pp. 450–468 (1939). Washington, D. C., U. S. Govt. Printing Office (1940).
51. Harshaw, H. M., *J. Agr. Research* **53**: 357 (1936).

52. Harshaw, H. M., and Rector, R. R., *Poul. Sci.* **19**: 404 (1940).
53. Hegsted, D. M., and Rao, M. N., *J. Nutrition* **30**: 367 (1945).
54. Hegsted, D. M., *J. Nutrition* **32**: 467 (1946).
55. Hegsted, D. M., Mills, R. C., Briggs, G. M., Jr., Elvehjem, C. A., and Hart, E. B., *J. Nutrition* **23**: 175 (1942).
56. Heuser, G. F., *Poul. Sci.* **20**: 362 (1941).
57. Heuser, G. F., Wilgus, H. S., and Norris, L. C., *Poul. Sci.* **17**: 105 (1938).
58. Heywang, B. W., *Poul. Sci.* **19**: 29 (1940).
59. Hinshaw, W. R., and Lloyd, W. F., *Hilgardia* **8**: 281 (1934).
60. Hogan, A. G., Richardson, L. R., Patrick, H., O'Dell, B. L., and Kempster, H. L., *Poul. Sci.* **20**: 180 (1941).
60a. Hogan, A. G., *Nutr. Absts. Rev.* **19**: 751 (1950).
61. Jaap, R. G., and Thayer, R. H., *Poul. Sci.* **23**: 249 (1944).
62. Jaap, R. G., and Thayer, R. H., *Poul. Sci.* **24**: 187 (1945).
63. Jeffrey, F. P., *N. J. Agr. Expt. Sta. Bull.* **656** (1938).
64. Jukes, T. H., *Poul. Sci.* **20**: 251 (1941).
65. Jukes, T. H., and Almquist, H. J., *Ann. Rev. Biochem.* **11**: 511 (1942).
66. Kempster, H. L., and Turner, C. W., *Poul. Sci.* **24**: 94 (1945).
67. Klose, A. A., Stogstad, E. L. R., and Almquist, H. J., *J. Biol. Chem.* **123**: 691 (1938).
68. Klose, A. A., and Almquist, H. J., *J. Biol. Chem.* **138**: 467 (1941).
69. Kratzer, F. H., Bird, F. H., Asmundson, V. S., and Lepkovsky, S., *J. Nutrition* **34**: 167 (1947).
70. Loewy, A., "Oppenheimers Handbuch der Biochem." 2nd ed. Vol. 6, part 2, pp. 125–278. Jena, Verlag von Gustav Fischer (1923).
71. Lorenz, F. W., *Poul. Sci.* **22**: 190 (1943).
72. Lorenz, F. W., *Poul. Sci.* **24**: 128 (1945).
73. Lorenz, F. W., and Bachman, G. H., *Poul. Sci.* **26**: 419 (1947).
74. Marble, D. R., Hunter, J. E., Knandel, H. C., and Dutcher, R. A., *Poul. Sci. Poul. Sci.* **17**: 49 (1938).
75. Maw, W. A., *Sci. Agr.* **16**: 77 (1935); see also Maw, W. A., Maw, A. J. G., and Holcomb, R., *Sci. Agr.* **19**: 597 (1939).
76. McClary, C. F., Bearse, G. E., and Miller, V. L., *Western Wash. Agr. Expt. Sta. Ann. Rept.* **45** (1939).
77. Miller, M. W., and Bearse, G. E., *Wash. Agr. Expt. Sta. Bull.* **306** (1934).
78. Motzok, I., Graham, W. D., Branion, H. D., and Slinger, S. J., *Poul. Sci.* **25**: 298 (1946).
79. Murphy, R. R., *Pa. Agr. Expt. Sta. Bull.* **429** (1942).
80. Murphy, R. R., Hunter, J. E., and Knandel, H. C., *Pa. Agr. Expt. Sta. Bull.* **303** (1934); **334** (1936).
81. Mussehl, F. E., and Ackerson, C. W., *Poul. Sci.* **14**: 147 (1935).
82. Mussehl, F. E., Ackerson, C. W., and Thayer, R. H., *Poul. Sci.* **20**: 469 (1941).
83. Nestler, R. B., *Trans. Eleventh. North American Wildlife Conference*, **176** (1946).
84. Nestler, R. B., *J. Wildlife Management* **10**: 137 (1946).
85. Nestler, R. B., Bailey, W. W., and McClure, H. E., *J. Wildlife Management* **6**: 185 (1942).
86. Norris, L. C., Elmore, L. J., Ringrose, R. C., and Bump, G., *Poul. Sci.* **15**: 454 (1936).
87. Norris, L. C., Heuser, G. F., Ringrose, A. T., and Wilgus, H. S., *Poul. Sci.* **13**: 308 (1934).

88. Poley, W. E., Moxon, A. L., Wilson, W. O., and Dolecek, R. L., *J. Agr. Research* **61**: 161, 179 (1940).

89. Record, P. R., and Bethke, R. M., *Poul. Sci.* **21**: 271 (1942).

90. Record, P. R., and Bethke, R. M., and Wilder, O. H. M., *Poul. Sci.* **16**: 25 (1937).

91. Ringrose, R. C., and Norris, L. C., *Poul. Sci.* **15**: 390 (1936).

92. Roberts, R. E., *Ind. Agr. Expt. Sta. Bull.* **448** (1940).

93. Rubin, M., and Bird, H. R., *Md. Agr. Expt. Sta. Bull.* **A12** (Tech.) (1942).

94. Rubin, M., Bird, H. R., and DeVolt, H. M., *Poul. Sci.* **20**: 155 (1941).

95. Russell, W. C., Platt, C. S., Taylor, M. W., and Chichester, D. F., *N. J. Agr. Expt. Sta. Circ.* **369** (1936).

96. Schaible, P. J., *Poul. Sci.* **20**: 278 (1941).

97. Sherwood, R. M., and Fraps, G. S., *Texas Agr. Expt. Sta. Bull* **468** (1932); **493** (1934; **514** (1935); **528** (1936); **583** (1940).

98. Skoglund, W. C., *Pa. Agr. Expt. Sta. Bull.* **389** (1940).

99. Sturkie, P. D., *Poul. Sci.* **25**: 365, 531 (1946).

100. Subcommittee on Poultry Nutrition, Recommended Nutrient Allowances for Poultry, Washington, D. C., Nat'l. Res. Council, 1944 (Rev. November 1, 1946, and March, 1950).

101. Tepper, A. E., and Durgin, R. C., *N. H. Agr. Expt. Sta. Bull.* **310** (1938).

102. Thayer, R. H., Jaap, R. G., and Penquite, R., *Poul. Sci.* **24**: 483 (1945).

103. Titus, H. W., *Poul. Sci.* **8**: 89 (1928).

104. Titus, H. W., "Food and Life" Yearbook of Agriculture 1939, pp. 787–843. Washington, D. C., U. S. Govt. Printing Office (1940).

105. Titus, H. W., "The Scientific Feeding of Chickens." 2nd ed. Danville, Ill., The Interstate Publishers and Printers, Inc. (1949).

106. Titus, H. W., Jull, M. A., and Hendricks, W. A., *J. Agr. Research* **48**: 817 (1934).

107. Waisman, H. A., Mills, R. C., and Elvehjem, C. A., *J. Nutrition* **24**: 187 (1942).

108. Watkins, W. E., and Mitchell, H. H., *Poul. Sci.* **15**: 32 (1936).

109. Wilgus, H. S., *Poul. Sci.* **10**: 107 (1931).

110. Wilgus, H. S., Harshfield, G. S., Patton, A. R., Ferris, L. P., and Gassner, F. X., *Poul. Sci.* **20**: 477 (1941).

111. Wilhelm, L. A., Robertson, E. I., and Rhian, M., *Poul. Sci.* **20**: 565 (1941).

112. Williams, J. K., Lampman, C. E., and Bolin, D. W., *Poul. Sci.* **18**: 268 (1939).

Chapter XVIII

THE NUTRITION OF SWINE

R. C. Miller

The Pennsylvania State College, State College, Pa.

It has been estimated that the cost of feed amounts to 80 per cent of the cost of pork production, this figure being dependent, of course, on relative prices. Swine will consume up to from 10 to 15 pounds of feed per day at the heavier weights or from 2.5–5.5 per cent of the body weight. Normally pigs should be marketed at a live weight of 200–225 pounds as it is at this weight that the degree of finish produced supplies the quality and weight of cuts desired by the consumer, and it is also at this weight that an economical return for feed cost is obtained. Beyond 200–225 pounds additional body gains are inefficiently produced on a per pound feed cost basis.

The gross calories in edible products obtained from pork represent about 20 per cent of the calories fed to pigs as compared to 15 per cent for the dairy cow. It requires approximately 7 pounds of feed to produce 2600 calories of human food in the form of pork.[20] This is a greater efficiency than is obtained with any other class of livestock. It should be said, however, that most of the feed consumed by pigs is in the form of concentrates, while with cattle, roughage, which is unsuitable for human consumption, constitutes the major portion of the feed.

The swine industry in the United States has been built around corn as the principal feed for pigs. As a rule, the relative prices of corn and pork have been such that usually it has been possible to market corn profitably by feeding it to swine. As a result it is common to think of hogs and corn almost synonymously. However, feed is but one of a number of factors which must be considered in a profitable swine enterprise. The control and prevention of disease, good breeding, proper management, and adequate nutrition are all related and are all important in contributing to a successful swine program. With the numerous advances made in the science of nutrition in recent years much has been learned about the nutrition of swine. However, there are many problems in the feeding of swine which are unsolved and it may be expected that much will be learned in the future along this line.

While swine are heavy consumers of home-grown feeds the commercial production of mixed pig feeds, particularly protein supplements, is an important industry. The types of commercial feeds available to the swine producer vary from protein concentrates and rather simple mixtures for replacement of locally produced grains, to complex mixtures supplying minerals, vitamins, and protein from numerous sources. Owing to the fact that the nutritive requirements of swine are different under different conditions, it is impossible to formulate one feed mixture which will be economical and completely satisfactory under all conditions.

In considering the nutritive requirements of swine it is now recognized that there are four periods in the life cycle of the pig, in which the nutritive requirements are distinctly different and rather exacting. These follow. (1) The gestation period in which feed must not only supply the nutrients required for the usual body functions of the sow, but also those essentials for the litter of pigs being nourished *in utero*. (2) The lactation or suckling period when the feed of the sow must be adequate to maintain a flow of milk which is sufficient for the litter of suckling pigs. Pigs are usually weaned at about eight weeks of age. (3) The early growth period, beginning at weaning time or previous to weaning, when the small pigs begin to eat feed in addition to the sow's milk, and lasting until the pigs have attained a body weight of 65 or 75 pounds. (4) The growing fattening period from 65–75 pounds up to a market weight of 200–225 pounds. In addition there may be special requirements for gilts, dry sows, boars, and all pigs used primarily as breeding stock.

The availability of pasture is a further complication in the problem of supplying the proper nutrients to swine. It is impossible at this time to duplicate completely in a dry feed the nutrients supplied by pasture. While much progress has been made in elucidating nutritive factors supplied by feedstuffs, it is altogether likely that pasture supplies some nutrients which as yet have not been identified. In this connection it is probable also that all types of pasture are not of equal value. The high nutritive qualities of alfalfa have been recognized for a long time, but more recently it has been found that ladino clover is particularly valuable for pigs as well as for other classes of livestock. Suitable methods are now lacking for the proper appraisal of the relative nutritive values of different pasture crops, and it is impossible at the present time to evaluate them accurately by means of existing methods of chemical analysis or vitamin assay.

In the past the main considerations in a swine feeding program were to provide suitable protein for growth and enough high energy feed to insure rapid fattening. The literature is full of reports of feeding trials dealing with suitable sources of supplementary protein. Outstanding among the protein mixtures found to be quite suitable for growing pigs is the so-called "trio" mixture which was developed at the Wisconsin Agricultural Experiment Station.[25, 27] This mixture is composed of 50 pounds of tankage, 25 pounds of chopped alfalfa or other legume hay, and 25 pounds of linseed meal and has been widely used. When fed with corn it is superior to corn and tankage alone, and has been recommended not alone because of its economy, but also because of the insurance it furnishes "against some of the pigs being made unthrifty or even becoming runts because of a lack of vitamins."[26] It should be emphasized at this point that swine feeders and nutritionists for the most part, have failed in the past to differentiate between protein and the vitamins, minerals and unknown factors which are supplied by crude protein carriers such as the trio mixture. Many of the results obtained in practical feeding and in experimental work have been attributed to protein, whereas they may be more logically explained by the other factors accompanying the protein of a particular feedstuff.

NUTRITIVE REQUIREMENTS

It is only comparatively recently that it has been possible to enumerate the dietary factors required by pigs. The list today is doubtless incomplete and in many instances the specific functions of many of the factors are unknown. Enough is known however, so that a swine ration may now be formulated on the basis of the nutrients it furnishes rather than the ingredients it contains, with the reasonable assurance that the requirements of the animals will be satisfied.

In Table 117 are given the daily nutrient allowances recommended for swine published by the Committee on Animal Nutrition of the National Research Council in 1944. A number of nutrients known to be needed by swine are not included in this table owing to a lack of quantitative data or of such data as are applicable to classes of pigs not covered by this table (suckling pigs). The respective nutrients will be discussed separately together with the specific requirements for these nutrients by certain classes of pigs.

CARBOHYDRATES

As has been mentioned, corn serves as the main source of carbohydrate for the swine industry. Corn may be fed as the only source of carbohydrate or it may be replaced in part by other grains including wheat, oats, barley, and sorghums.

The pig is unique among all animals for the physiological mechanism whereby it can readily convert carbohydrate into body fat. Thiamin, which is necessary for this transformation of carbohydrate to fat, is found in pork muscle in much larger amounts than is present in the tissues of other species.[22]

Owing to the nature of its digestive tract the pig must be fed a concentrated ration as compared to animals that can digest large amounts of roughage. A bulky ration containing large amounts of fiber necessarily contains less of the nutrients required for rapid gains and is, therefore, uneconomical for pigs. With growing-fattening pigs the fiber content should not exceed 5–8 per cent. However, with mature pigs and with breeding animals a fiber content of 10 per cent is permissible and desirable in most instances.

TABLE 117. DAILY NUTRIENT ALLOWANCES RECOMMENDED FOR SWINE

	Growing, Fattening Pigs Live Weight, Lb.					Pregnant Gilts and Sows; Young Boars	Lactating Sows; Breeding Boars
	50	100	150	200	250		
Daily expected gain, lb.	0.90	1.50	1.75	1.80	1.80	0.75 [min.]	
Total feed [air dry basis], lb.	2.7	5.0	6.6	7.5	8.3	6.0	10-15
Equivalent T.D.N., lb.	2.0	3.8	5.0	5.6	6.2	4.5	7.5-11.3
Crude protein, lb.	0.6	0.8	0.9	1.0	1.0	0.9	1.5-2.3
Inorganic nutrients							
Calcium, g.	7.4	13.7	15.8	17.9	17.9	16.4	27-41
Phosphorus, g.	4.9	9.1	10.5	11.9	11.9	10.9	18-27
Sodium, g.	2.7	5.0	6.6	7.5	8.3	6.0	12.5
Potassium, g.	1.3	2.5	3.8	5.0	6.0	6.0	12.5
Vitamins							
Carotene, mg.	2.0	4.0	6.0	8.0	10.0	20.0	40.0
Vitamin A, I.U. [Thousands]	1.3	2.6	3.9	5.2	6.5	13.0	26.0
Vitamin D,	135	250	330	375	415	300	625
Thiamine, mg.	1.4	2.5	3.3	3.8	4.2	3.0	6.3
Riboflavin, mg.	2.1	3.8	5.0	5.7	6.3		----
Niacin, mg.	7.0	12.5	16.5	19.0	21.0		----
Pantothenic acid, mg.	10.0	18.5	----	----	----		----
Pyridoxine, mg.	1.6	3.0	----	----	----		----

Vitamin D: This requirement may be fully met by ultraviolet radiation from the sun.

Thiamine: Amounts specified will permit development of a normal pig but will not provide for thiamine storage.

Vitamin E: Required, but amounts unknown.

Iron: Requirements beyond weaning unknown. For suckling pigs 15 mg. iron daily for first three weeks will maintain hemoglobin level.

Copper: Usually taken as 5% of the iron administered.

Cobalt: For sheep, 4 oz. $CuSO_4$ per ton NaCl has been enough to reduce deficiency symptoms. Swine requirements unknown.

Iodine: For pregnant sows, 0.2 mg. iodine per 100 lb. body weight has been proposed. Requirements for other swine are probably somewhat less.

Magnesium + Manganese + Zinc: Required, but amounts unknown.

Most feeds commonly used for pigs are relatively low in fiber content but feeds such as oats, wheat bran, and corn and cob meal must be used in limited amounts owing to their higher content of fiber. Owing to its content of vitamin A and other factors alfalfa hay is used in many swine feeds. The upper limit of good quality alfalfa that may be used in rations for brood sows is approximately 20 per cent, and 10–12 per cent of alfalfa is frequently used in rations for pigs. These amounts of alfalfa will not cause any difficulty if the hay is leafy, but if it is high in fiber content such amounts are unsuitable and will not fulfill the purpose for which their use is intended.

FAT

Dietary fat for the pig may not necessarily be an important economic consideration as a source of energy for swine, but it is important in relation to the type of fat laid down on the carcass of the pig. Soft pork results from the feeding of such feeds as peanuts and soybeans which contain relatively large amounts of unsaturated fatty acids with low melting points. The fat on the carcasses of pigs fed these feeds is correspondingly soft, and the fresh and cured products from such hogs are undesirable and difficult to handle. The carcass is flabby, fresh cuts do not hold their shape and the lard is oily in nature and has poor keeping qualities.

The fat in the diet of the hog is apparently transformed directly to tissue fat and retains the chemical characteristics of the food fat. On the other hand, body fat which is produced by the conversion of carbohydrates or protein is apparently hard in nature.[10] Owing to the fact that fat is normally soft at the temperature of the body irrespective of its chemical composition, it is impossible to distinguish a soft killing hog before slaughter. This presents a difficult problem to the buyer who will discriminate against soft pork if possible.

Certain feedstuffs, notably cottonseed meal, produce firm, hard pork and may be used in a feeding program in connection with peanuts or other feeds producing soft pork.[12, 13] It is recommended that feeds such as peanuts be fed only until pigs weigh 90–100 pounds; thereafter, cottonseed meal is fed in amounts of about 15 per cent, in combination with corn and tankage, until a finished body weight of 200–225 pounds is attained. Corn alone is considered as a hardening feed.

The carcass grade, as established by a competent judge, is used for evaluating pork carcasses for softness. This grade may be correlated with the refractive index, the iodine number, or the melting point of the body fat.

PROTEIN

Success in swine feeding may depend in large part on how well the protein requirements are satisfied. Mention has been made of the trio mixture as a protein supplement. At the present time proteins in general are the subject of much critical study with regard to their constituent amino acids. Little is known of the specific requirements of pigs for individual amino acids. Of the approximately 21 known amino acids it is assumed that at least 10 of these are indispensable for growing pigs and must be supplied in the feed.

The practical solution of the problem of supplying the indispensable amino acids required by swine has been to supply protein in the feed from several sources, at least one of which is protein of animal origin, such as fish meal or tankage. This protein mixture is frequently fed separately as a supplement to corn or other grain. When given feed free choice in self feeders pigs do a good job of balancing their own diet, and will consume amounts of feed closely approximating their requirement for nutrients such as carbohydrates and protein.

The protein requirements of growing fattening pigs in total swine rations have been determined to be approximately as follows: [21]

	%
From weaning to 70 lb.	22
From 70 to 125 lb.	17–20
From 125 to 200 lb	15
Over 200 lb.	12–13
Bred sows	14–15
Nursing sows	15–16

These figures pertain to feeding in dry lot; in general 3 per cent less of protein will be required in the grain-supplement mixture when the pigs also have access to good pasture. Some idea of the upper limit of protein required by pigs may be gained by considering that sows' milk, which may be supposed to constitute the ideal food for baby pigs contains on a dry basis approximately 31 per cent of protein which is of good quality with respect to its amino acid pattern. In contrast corn contains 8.5–9.0 per cent of protein of lower quality with respect to amino acids, and cannot be depended on as the sole source of protein for pigs of any class.

In recent years soybeans and soybean products have been used extensively in swine feeding. As has been mentioned the feeding of whole soybeans is conducive to soft pork. Soybean oil meal, however, is an excellent source of protein for pigs and has a high biological value if the soybeans have been properly treated with heat during processing. It was first discovered in 1917 that cooked soybean meal was superior to the raw meal for the growth of rats.[28] It appears that the beneficial effect of heat treatment in some way improves the availability of the sulfur-containing amino acids in soybeans. Inadequately heated soybean oil meal, therefore, is inferior in its protein value for pigs. Appearance and taste of soybean meal are not dependable criteria for evaluating its previous heat treatment; however, a test for urease gives promise of being useful for this purpose.[3]

Corn protein has been recognized for many years as being relatively deficient in the amino acids lysine and tryptophane. It has recently been discovered that the niacin requirements of pigs, and of certain other growing animals, is higher when they are fed relatively low protein diets which are high in corn content.[16, 17, 18, 31] Niacin deficiency, when induced by the feeding of high corn diets, is alleviated by the administration of either niacin or the amino acid tryptophane, thus establishing for the first time a unique amino acid vitamin relationship. At first it was believed that corn contained a deleterious factor responsible for an increased requirement of the animal for either niacin or tryptophane, but this viewpoint is rather generally discounted since the deficiency has been induced by other protein combinations not containing corn. Experiments with rats now indicate that the depression of growth obtained on corn and on other niacin low diets may be attributed to an imbalance of amino acids.

Sufficient information is not now available on the requirements of pigs for individual amino acids, or on the amino acid content of feedstuffs so that feed mixtures can be recommended which will be certain to satisfy the needs of the animal in every detail. There is sufficient information available, however, to state that any single protein supplement will probably not be economical and satisfactory for pigs of all classes.

The protein requirements of an animal should be considered in relation to its physiological needs, these being far different for a young growing pig, a lactating sow, or a fattening gilt. The previous nutritional treatment of the animal also has a bearing on its protein requirements.

The newer conception of protein metabolism is that there is a state of dynamic rather than static equilibrium in the body. In times of stress certain tissues may be depleted of protein in order to maintain normal body functions. Protein starvation may be induced by an improper dietary pattern of amino acids in spite of an otherwise adequate gross protein intake. An imbalance of ingested amino acids may result in protein depletion of tissues in order to maintain normal metabolism. It is quite often apparent in lactating sows that, in spite of an apparently adequate feed intake, the body tissues are depleted in order to satisfy the high demands of lactation. When more is learned of specific amino acid requirements it will be possible to fulfill these requirements more nearly by the selection of feeds supplying the appropriate pattern of amino acids.

VITAMINS

Vitamin A. Swine fed in dry lot without access to pasture, on rations made up largely of grains other than yellow corn, may develop vitamin A deficiency. Unlike some of the other vitamins, vitamin A may be stored in the body, the liver being the site of this storage. In times of stress the animal can utilize its body stores of vitamin A, thus a deficiency results usually after a rather prolonged period of vitamin A insufficiency in the diet.

Vitamin A deficiency in swine may affect the eyes and the locomotion, the manifestations being night blindness and lameness. Other symptoms may be slow growth, impaired appetite, diarrhea, a rough hair coat, impaired breeding, and weak or dead pigs at birth. A crooked back sometimes occurs in growing pigs on vitamin A deficient diets when they attain a weight of 100–125 pounds. This is a permanent deformity which, apparently, does not greatly impair the animal otherwise.

It appears that all degrees of vitamin A deficiency may occur in pigs. In many instances moderately deficient pigs may continue to grow slowly. Sows may abort or the fetuses may be absorbed, or weak pigs may be produced. It is unlikely that uncomplicated vitamin A deficiency occurs frequently, the diet usually being deficient also in other respects. Green pasture, yellow corn, and ground alfalfa in dry-lot rations will prevent the occurrence of the deficiency. However, yellow corn may vary widely in its content of carotene which is the precursor of vitamin A. White capped corn is low in carotene content. Green feed is the best insurance against vitamin A deficiency.

Vitamin D. This vitamin is discussed in the section dealing with calcium and phosphorus on page 467.

Thiamin. Much of the experimental work that has been done with the water-soluble vitamins has been carried out with pigs fed purified synthetic diets. The need of the pigs for these factors has been established by this work but the practical significance of the results has been of limited application in most instances.

This is true of thiamine. It has been found that practical swine rations almost always contain sufficient thiamine for the pig. In addition to this it has been shown that thiamine in the ration,[22] in excess of the minimum required by the pig for normal metabolism, is stored in the muscle tissue. Mention has been made of the relatively high thiamine content of pork as compared to beef and meat from other species. It is doubtful if this extra thiamine is of any particular benefit to the pig but it does enhance the value of pork in the human dietary.

Red peanut skins are very high in thiamine content as compared to most feedstuffs and are valuable for pigs, supplying in addition considerable protein and fat.

Niacin. The work of Chick and associates [4] established the need of the pig for niacin. Reference has been made in the section on proteins to niacin-amino acid relationships discovered more recently.

While it is recognized that niacin is essential in the diet of the pig, the exact role played by niacin has not been fully elucidated. From observations in the field [19] and from experimental work [8] it has appeared that niacin deficiency might be one of the factors involved in the occurrence of necrotic enteritis of pigs. The clinical symptoms of necrotic enteritis, sometimes called necro, are a loss of appetite, depression of growth, diarrhea, high mortality, and necrotic lesions in the intestinal tract of the pig. These are almost the identical symptoms obtained in cases of niacin deficiency produced experimentally. Necrotic enteritis, however, has been considered to be an infectious disease attributed to the organism *Salmonella choleraesius*. This disease usually responds to treatment by sulfa drugs and in some instances niacin administration has been beneficial, but niacin treatment of experimentally infected pigs has not been effective.[9]

It appears to be possible that an uncomplicated niacin deficiency may occur in pigs under some practical conditions. It is possible that in some practical rations an amino acid imbalance, which increases the pigs' niacin requirement, may be in large part responsible for this condition rather than an actual deficiency of niacin in the feed. This does not preclude the occurrence of the infectious type of enteritis, the susceptibility for which, however, may be predisposed by the same dietary influences.

Vitamin B_{12} (APF). This is the newest member of the vitamin family found to be of importance in swine nutrition.[10a] Isolated in pure crystalline form in 1948, this vitamin is a complex organic compound containing phosphorus and cobalt. It has been supplied in the past in practical rations from animal protein sources such as fish meal, tankage, and milk products. It is now produced commercially as a primary product or as a by-product of fermentation and is available to the feed industry in the form of APF (animal protein factor) supplements. Thus there has been made available to the feed manufacturer and the feeder a concentrated form of this factor heretofore supplied only by natural sources of animal protein. While only a limited amount of research has been conducted with vitamin B_{12} it appears that APF products containing B_{12} will be of value in supplementing protein from plant sources in swine rations[3a, 3b]. It seems improbable that APF supplements containing B_{12} may entirely replace natural sources of animal protein in swine feeds, but it appears that less animal protein from usual sources may be required when APF supplements are used in the ration.

In conjunction with the development of APF supplements it has been discovered that under certain conditions some of the antibiotic drugs, notably aureomycin and streptomycin, have very striking growth-promoting properties for swine.[11a] The possible place of these materials in a feeding program is unpredictable in view of the limited amount of research to date in this field.

Other B-Complex Vitamins. Considerable experimental work has been conducted with purified rations which indicates that a number of the B-complex vitamins are essential for the pig, but there is still a lack of evidence dealing with specific deficiencies of these nutrients when pigs are fed natural feeds. This is not to say that combinations of natural feedstuffs always adequately supply these factors, evidence on this point being to the contrary.[11] The inadequacies of natural rations, however, have not been completely determined and it is commonly held that factors as yet unidentified are required by pigs. The factor or factors thus in question are not supplied by the grains or by grain by-products. Pasture and high quality alfalfa, distillers and fermentation solubles, fish solubles, and milk by-products supply the unknown factors and may be used to excellent advantage in practical swine rations.

Among the factors known to be required by pigs are riboflavin[14] (1–3 mg. daily per 100 pounds body weight), pantothenic acid, and pyridoxine. The latter compounds are probably necessary in order to maintain a normal nervous system in the pig.[31] The essentiality of biotin has been demonstrated for the pig by producing a biotin deficiency by the feeding of desiccated egg white in the ration.[7] There may not be sufficient evidence to prove the essentiality of choline, inositol, and pteroyl glutamic acid, but until disproved they should be considered to be essential for the pig.

Mineral Nutrition

Thirteen mineral elements are now known to be indispensable in animal nutrition.[23] They are: sodium, potassium, calcium, magnesium, iron, manganese, phosphorus, chlorine, sulfur, iodine, copper, cobalt, and zinc. This discussion will be limited to certain of these mineral elements which are ordinarily not supplied in sufficient amounts by swine feeds, or for which swine have unusual demands. Potassium and magnesium are present in feeds in amounts adequate for all known purposes. This is also true for sulfur and zinc. Cobalt, known to be important in ruminant nutrition has not been shown to be necessary for pigs. Copper, iron, cobalt, zinc, manganese, and iodine are often referred to as trace minerals since although they are important, they are required in very small amounts.

Sodium and Chlorine. Ordinary swine feeds do not contain enough sodium and chlorine to permit the maximum utilization of these feeds by pigs. Common salt must therefore be supplied to provide chlorine for gastric secretion and sodium chloride for certain body fluids. Salt may be fed free choice to pigs or it may be mixed in the feed in amounts from 0.25 to 1 per cent. It is often more convenient to feed salt mixed with other minerals that are being fed free choice thereby allowing the pig to govern his own intake of these essential elements.

Calcium, Phosphorus, and Vitamin D. Vitamin D will be discussed together with calcium and phosphorus because of the interrelationships of these three factors particularly in the metabolism of bone. The pig is a very fast growing animal and has relatively high requirements for bone building elements. Calcium, phosphorus, and vitamin D may all be limiting factors for growth and calcification of bone.

The grains commonly fed to pigs contain but little calcium but do supply a fair amount of phosphorus. On the other hand, fish meal, meat scrap, and tankage supply more calcium than phosphorus. Vitamin D may be obtained by the pig through the direct action of sunlight or by vitamin D carrying supplements. The only natural feed source of vitamin D for pigs is hay that has been cured with a proper exposure to sunlight.

Rickets is the usual manifestation of a deficiency of any of the bone forming elements or of improper proportions of calcium to phosphorus. This disorder is characterized clinically by faulty calcification of the bones and results in lameness of the pig, which formerly was sometimes called posterior paralysis. When severely afflicted, the pig is very often unable to rise to its feet and can walk only with great difficulty. These outward mainfestations appear particularly in the leg bones although the entire skeleton is affected. Pathologically there develops a wide cartilagenous area at the zone of provisional calcification. The leg joints of the pig become enlarged, the bones themselves are low in mineral content and are relatively soft. Rapidly growing pigs are most frequently affected, and if the dietary deficiency is not corrected they will die.

The important considerations in preventing rickets in pigs are to supply sufficient amounts of vitamin D, calcium, and phosphorus, it being necessary also to supply the latter in proper proportions. It has been established that, in the absence of added vitamin D, the ration should contain 0.60 per cent of phosphorus. The ratio of calcium to phosphorus should be between 1.0 and 2.0 : 1.[1] The minimum vitamin D requirements of the growing pig fed approximately 0.60 per cent calcium and 0.45 per cent phosphorus is of the order of 90 U.S.P. units per pound of feed,[2] practical allowances, however, usually exceeding this amount.

If pigs are given feed containing calcium and phosphorus in an improper ratio such as greater than 3 : 1, the effect on calcification may be much the same as if the ration was actually deficient in these elements. There is also some evidence to show that with an improper calcium phosphorus ratio the vitamin D requirements of the pig are increased.

Apparently pigs are able to use either the 7-dehydrocholesterol, D_3, or the calciferol, D_2, forms of vitamin D and supplementary vitamin D may be supplied directly in the ration in the form of fish oil or irradiated yeast. It is unlikely, however, that pigs require any supplementary vitamin D if they are exposed to sunlight and are receiving liberal amounts of calcium and phosphorus. Supplementary vitamin D added to the ration will be advantageous, however, for pigs confined to inside quarters, and to baby pigs farrowed in the late fall, winter, or early spring when the whether is cold and solar radiation is weak.

Reasonably liberal amounts of vitamin D in excess of the minimum requirements may be supplied to pigs without any harmful effects; in fact, there is some evidence to show that such amounts of vitamin D are conducive to slightly more rapid body gains and aid in conserving feed.

Swine rations must usually be supplemented with calcium and phosphorus in order to supply these elements in sufficient amounts and in the correct proportion. Ground limestone and bone meal are the two materials most commonly used for this purpose and are generally recommended. Table 118 gives the composition of a number of calcium and phosphorus supplements suitable for animal feeding.

TABLE 118. COMPOSITION OF CALCIUM AND PHOSPHORUS SUPPLEMENTS *

Mineral Supplement	Calcium %	Calcium G. per Lb.	Phosphorus %	Phosphorus G. per Lb.	Fluorine %
Bone meal, raw, feeding	22.7	103	10.1	46	0.030
Bone meal, special steamed	28.7	130	13.9	63	-----
Bone meal, steamed	30.0	136	13.9	63	0.037
Defluorinated phosphate rock a[1]	21.0	95	9.0	41	0.15 or less
Defluorinated phosphate rock b[1]	29.0	132	13.0	59	0.15 or less
Defluorinated superphosphate	28.3	128	12.3	56	0.15 or less
Dicalcium phosphate	26.5	120	20.5	93	0.05
Disodium phosphate	----	---	8.6	39	----
Limestone	38.3	174	----	--	----
Monocalcium phosphate	16.0	72	24.0	109	0.05
Monosodium phosphate	----	---	22.4	102	----
Oyster shell flour	36.9	167	---	---	----
Spent bone black	22.0	100	13.1	59	----

* Because of the limited number of products on the market, figures are given for two types of defluorinated rock which are being produced for livestock feeding.

Ref.: "Recommended Nutrient Allowances for Beef Cattle," Report of the Committee on Animal Nutrition, National Research Council, September 1943.

Calcium and phosphorus may be given to swine free choice in a self feeder, or they may be mixed in the feed. When offered in a self feeder they are commonly mixed with equal parts of salt, but they may be offered separately if they are being consumed in amounts to satisfy the pigs' requirements. Vitamin D in the form of irradiated yeast may be mixed with these minerals without any great loss of the vitamin over a period of a number of weeks. However, vitamin D in the form of fish oil is unstable and cannot be mixed with the minerals.

In addition to its importance as a bone forming element phosphorus plays a very important role as a component of systems involved in metabolism in the body.[24] Phosphorus as it occurs in the soft tissues aids in the storage and transfer of energy through the process known as phosphorylation. Thus fullest utilization of the feed may be limited by a phosphorus deficiency. Whereas in time of high demand, calcium can be withdrawn from the skeleton to satisfy unusual demands, phosphorus apparently cannot be thus mobilized and must be continuously supplied in the feed in amounts that are adequate for all purposes.

Iron and Copper. Suckling pigs are frequently affected with nutritional anemia commonly known as *thumps*. This deficiency is due to a lack of iron, copper, and possibly other elements necessary for the formation of blood hemoglobin, and usually affects pigs which are confined indoors for more than a week or ten days after birth. The coats of the pigs become rough, the skin pale, and the breathing becomes labored in an effort to obtain sufficient oxygen. Unless therapeutic measures are taken the pigs die.

The pig is born with a reserve supply of iron, mostly in the liver, to tide it over the suckling period. The extent of this reserve will often determine whether or not the pig becomes anemic. The milk of the sow is low in iron content and cannot be increased by feeding iron to the sow. The problem, therefore, is to supply the pig with the highest possible iron reserve at birth and to furnish means of obtaining additional iron at an early age.

One solution of this problem is to supply iron and copper in the feed of the sow during the entire gestation period, and to make these minerals available to the suckling pig in the creep where they may be obtained at an early age.

Suckling pigs may also be drenched with a 2–5 per cent solution of a soluble iron salt such as iron sulfate containing also traces of copper. An alternative is to paint the udder of the sow with this solution so that the pigs may obtain the iron when they suckle.

Pigs that are outdoors on the ground are not so frequently affected with anemia since they may obtain some iron and copper from the soil. Clean soil, in the sense that it does not contain the eggs of parasites, may be placed in the pens of suckling pigs confined indoors and thus supply them with iron and copper. This practice involves the risk, however, of introducing parasites present in the soil.

The solution of the anemia problem in pigs is so simple that this disease should not be of much economic importance, but owing largely to neglect, it takes a large toll of young pigs every year. Iron and copper are the two mineral elements primarily involved but other so-called trace elements may play a role in the disease. Where precautions are taken to supply these necessary minerals to sows and young pigs, little trouble is encountered even with pigs which are continually confined as is the practice in many commercial operations. Preventative rather than therapeutic measures are to be preferred since anemia, although finally overcome, may impair or handicap pigs previously affected.

Iodine. Iodine is necessary for the formation of thyroxin, the active principle of the thyroid gland. A deficiency of iodine in farm animals usually results in the occurrence of goiter, but in the case of swine, hairlessness of new-born pigs is a frequent manifestation of iodine deficiency.

Iodine must be supplied to the animal continuously for the normal functioning of the thyroid gland, but apparently increased demands for iodine accompany pregnancy. The question of supplying adequate amounts of iodine to swine is a geographical problem since an iodine deficiency in the soil, water and crops occurs mainly in the so-called goiter belt of the Northwest and the Great Lakes section. The feeder in these areas must supply additional iodine to farm animals and the feed manufacturer who distributes feedstuffs in these areas should also take this precautionary measure.

The amount of iodine required by swine is small and is easily supplied in the form of iodized salt. Potassium iodide in amounts of about 1 to 1.5 ounces per ton of feed may be used in mixed feeds.

Fluorine. Fluorine is important in livestock nutrition because of its severe toxicity when it occurs in more than trace amounts in the feed. Very minute amounts of fluorine are thought to be necessary for the proper development of teeth and bones, but larger amounts are definitely injurious to these tissues. The same harmful effects may occur as a result of the continuous ingestion of even small amounts of fluorine: these apparently are deposited and accumulate in the teeth and bones.

In fluorine poisoning the bones are weakened and become thick and soft. Similar gross changes occur in the teeth which eventually become worn down to the extent that proper mastication of feed is impossible. In young animals the enamel of the teeth develops improperly and becomes mottled.

Rock phosphates which might otherwise be used rather indiscriminately as sources of phosphorus for livestock, almost invariably contain amounts of fluorine which are harmful unless the rock phosphate is defluorinated to remove some of this injurious element. It will be noted that several of these defluorinated phosphates are included in Table 118. The use of these defluorinated products became widespread during the war when only limited supplies of bone meal were available. Their use in amounts to give a concentration of 0.01 per cent of fluorine in the total dry ration of swine is now accepted. This amount of fluorine being thought to be borderline between a safe and an unsafe level of fluorine for this species.[6]

BIBLIOGRAPHY

1. Bethke, R. M., Edgington, B. H., and Kick, C. H., *J. Agr. Research* 47: 331 (1933).
2. Bethke, R. M., Burroughs, W., Wilder, O. H., Edgington, B. H., and Robison, W. L., *Ohio Agr. Expt. Sta. Bull.* 667 (1946).
3. Bird, H. R., Boucher, R. V., Caskey, C. D., Jr., Hayward, J. W., and Hunter, J. E., *J. Assoc. Official Agr. Chem.* 30: 354 (1947).

3a. Catron, D., and Culbertson, C. C., *Iowa Farm Sci.* 3: 3 (1949).

3b. Catron, D., and Wallace, J. J., *Iowa Farm Sci.* 4: 19 (1949).

4. Chick, H., Macrae, T. F., Martin, A. J. P., and Martin, C. J., *Biochem. J.* 32: 10 (1938).

5. Committee on Animal Nutrition, Nat'l. Res. Council, Recommended Nutrient Allowance for Domestic Animals, II (1944).

6. Committee on Animal Nutrition, Nat'l. Res. Council, *Report* **10** (1943).

7. Cunha, T. J., Lindley, D. C., and Ensminger, M. E., *J. Animal Sci.* **5**: 217 (1946).

8. Davis, G. K., Freeman, V. A., and Madsen, L. L., *Mich. Agr. Expt. Sta. Tech. Bull.* **170** (1940).

9. Edgington, B. H., Robison, W. L., Burroughs, W., and Bethke, R. M., *J. Am. Vet. Med. Assoc.* **101**: 103 (1942).

10. Ellis, N. R., *J. Oil Fat Industries* **3**: 437 (1926).

10a. Folkers, K., *Chem. Eng. News* **28**: 1634 (1950).

11. Hogan, A. G., and Johnson, S. R., *Mo. Agr. Expt. Sta. Res. Bull.* **321** (1940).

12. Hostetler, E. H.,, Halverson, J. O., and Sherwood, F. W., *N. Carolina Agr. Expt. Sta. Tech. Bull.* **61** (1939).

13. Hostetler, E. H., and Halverson, J. O., *N. Carolina Agr. Expt. Sta. Tech. Bull.* **63** (1940).

14. Hughes, E. H., *J. Nutrition* **20**: 233 (1940).

14a. Jukes, T. H., Stokstad, E. L. R., Taylor, R. R., Cunha, T. J., Edwards, H. M., and Meadows, G. B., *Arch. Biochem.* **26**: 324 (1950).

15. Keith, T. B., and Miller, R. C., *Pa. Agr. Expt. Sta. Bull.* **401** (1940).

16. Krehl, W. A., Henderson, L. M., de la Huerga, J., and Elvehjem, C. A., *J. Biol. Chem.* **166**: 531 (1946).

17. Krehl, W. A., Sarma, P. S., and Elvehjem, C. A., *J. Biol. Chem.* **162**: 403 (1946).

18. Luecke, R. W., McMillan, W. N., Thorp, F., and Tull, Carolyn, *J. Nutrition* **33**: 251 (1947).

19. Madison, L. C., Miller, R. C., and Keith, T. B., *Science* **89**: 490 (1939).

20. Maynard, L. A., *J. Nutrition* **32**: 345 (1946).

21. Miller, R. C., Keith, T. B., Thorp, W. T. S., and McCarty, M. A., *Pa. Agr. Expt. Sta. Bull.* **449** (1943).

22. Miller, R. C., Pence, J. W., Dutcher, R. A., Ziegler, P. T., and McCarty, M. A., *J. Nutrition* **26**: 261 (1943).

23. Mitchell, H. H., and McClure, F. J., *Bull. Nat'l. Res. Council* **99** (1937).

24. Mitchell, H. H., *J. Animal Sci.* **6**: 365 (1947).

25. Morrison, F. B., Bohstedt, G., and Fargo, J. M., *Wisc. Special Circ.* (December 1922).

26. Morrison, F. B., "Feeds and Feeding." Ithaca, New York, The Morrison Publishing Co. (1936).

27. Morrison, F. B., and Fargo, J. M., *Wisc. Agr. Expt. Sta. Bull.* **352** (1923).

28. Osborne, T. B., and Mendel, L. B., *J. Biol Chem.* **32**: 369 (1917).

29. Pence, J. W., Miller, R. C., Dutcher, R. A., and Ziegler, P. T., *J. Animal Sci.* **4**: 141 (1945).

30. Wintrobe, M. M., Stein, H. J., Follis, R. H., Jr., and Humphreys, S., *J. Nutrition* **30**: 395 (1945).

31. Wintrobe, M. M., Miller, M. H., Follis, R. H., Jr., Stein, H. J., Mushatt, C., and Humphreys, S., *J. Nutrition* **24**: 345 (1942).

Chapter XIX

THE NUTRITION OF DOMESTIC AND FUR-BEARING ANIMALS

ARNOLD E. SCHAEFER

Alabama Polytechnic Institute, Auburn, Alabama

The study of the nutritional requirements of domestic animals has greatly enhanced man's knowledge in the field of human nutrition. The dog was one of the first experimental animals to be used in fundamental studies in physiology and biochemistry. Even before the first century an experiment using the dog is recorded which describes the early observations on food consumed in relation to total excreta. Since the nutritional requirements of the dog have been more extensively studied than other domestic and fur bearing animals, the first portion of this chapter is devoted mainly to a discussion of canine nutrition.

Consolidation of the voluminous information available on the nutritional requirements of the dog has been provided by very few texts or reviews. McCay's [49] book on ''The Nutrition of the Dog'' is the only recent text of its kind, and accomplishes much toward the application of the technical data to the practical aspect. The review article by Michaud and Elvehjem [58] is a concise summary of the nutritional requirements of the dog obtained from experimental data up to 1944. Koehn [37] has contributed much toward the formulation and testing of practical and commercial dog foods.

In any attempt to establish exact nutritive requirements, it must be borne in mind that any specific quoted value is subject to variation depending upon the size, age, activity of the animal, and lactation or pregnancy.

CALORIC REQUIREMENT

A general review of the caloric requirements for maintenance of mature dogs was summarized by Arnold and Elvehjem.[5] Dechambre (quoted by Linton) [44] compiled a table that lists the energy requirements of dogs for maintenance and undergoing moderate and hard work. Brody et al.[13] published food maintenance prediction tables based on body weight which were calculated from studies on basal metabolism, endogenous urinary nitrogen, and neutral sulfur excretion. In general, a 7-kg. dog requires approximately 75 to 80 calories per kg. of body weight, or 150 g. of dog food (dry basis) for maintenance, and a 20-kg. dog requires approximately ¾ to 1 pound of dry dog food.

Growing puppies require approximately twice as many calories per kg. of body weight as mature dogs.[6] Lactating females also need 2 to 3 times the total amount of food as do resting females. The requirement for pregnancy is not so great during the early stages as that required for lactation.

Each dog must be considered as an individual and the response in body weight should serve as a good index. Provided the diet is nutritionally adequate, if the animal loses weight the caloric intake should be increased and vice versa.

CARBOHYDRATE REQUIREMENT

Physiologically the ration for a dog should contain appreciable amounts of carbohydrate. Linton [44] suggested that the average diet for canines should consist of the following: 70 carbohydrate, 22 protein, 5 fat, 0.5 fiber, and 2.5 ash. These figures are in close proximity with the many experimental purified dog rations used. No specific amount has been determined as essential and numerous workers have used from 12.5 [23] per cent to 77 per cent [72] sucrose with equally good results.

Although the dog is classified as a carnivore, it digests both cooked and raw starch [71] even in amounts up to 62 per cent of the ration.[33] The saliva of the dog was long considered to be free of starch digesting enzymes, but Roseboom and Patton [70] credit it with amylolytic properties nearly equal to that of pancreatic juice. This observation was substantiated by Handelsman et al.[29] who observed that pancreatectomy hardly affected the degree of absorption of carbohydrates.

Koehn [37] fed a ration composed of 35 per cent yellow cornmeal, 10 per cent wheat bran, 20 per cent wheat shorts supplemented with alfalfa leaf meal, skim milk powder, meat scraps, bone meal, and salts to 12 brood bitches over a period of 3½ years. The animals thrived on this ration with some bitches producing as high as 7 litters of 10 healthy pups each.

Lactose fed as such is digested less efficiently than sucrose; however, dogs have been successfully carried through several generations on mineralized milk diets.[3]

FAT REQUIREMENT

Dogs can be maintained on diets containing relatively small amounts of fat. Recent observations by the Wisconsin group [72] show that puppies fail on a fat-free diet. A purified diet consisting of 77 per cent sucrose, 19 per cent casein, and 4 per cent salt mixture supplemented with ample amounts of thiamine, riboflavin, niacin, pantothenic acid, pyridoxine, choline and vitamins A and D, supported growth for 5 to 7 weeks. Rapid failure ensued which was characterized by loss in body weight, anemia, dusty hair coat, and death. This deficiency syndrome could not be alleviated by the feeding of corn oil (as a source of linoleic acid), corn oil plus folic acid, folic acid alone, vitamins E, K, inositol, *p*-aminobenzoic acid, biotin or ascorbic acid. Dramatic cures were obtained by feeding butterfat plus folic acid. Butterfat alone did not cure the deficiency. This interrelationship of butterfat and folic acid is most interesting and perplexing. It indicates that complete removal of fat from the diet of a growing pup disturbs some metabolic process that cannot be corrected by the feeding of any fat at random choice. The possible relationship between folic acid and a constituent of butterfat, such as specific fatty acids, is extremely interesting but without explanation at present.

Most experimental rations which have proved satisfactory for growth and maintenance contain 5 per cent to 11 per cent fat. Under conditions of extremely hard work, increasing the level of fat to 20 per cent to 30 per cent [91] may be the most effective and economical means of supplying the increased caloric requirement. In raising the fat level of the diet, it is important that a proper relationship exists between the amount of available energy and the amount of protein, minerals, and vitamins furnished by the diet.

PROTEIN REQUIREMENT

Magendie [48] in 1816 found that dogs fed a diet of gelatin preferred to die after a few days rather than eat the diet. Kaufman [35] feeding gelatin supplemented with tryptophan, cystine, and tyrosine noted that his animals thrived and remained in positive nitrogen balance for some time and then died. It is now known [69] that dogs will survive on a mixture of amino acids, as the sole source of protein, of the following: tryptophan, lysine, histidine, phenylalanine, leucine, isoleucine, threonine, methionine, and valine. Arginine [47] and possibly glycine [43] must be added for blood regeneration.

Lössel [45] concluded that a nutritive ratio of 1 to 4, (1 calorie from protein to every 4 calories from nonprotein food) was sufficient for optimum growth of small breeds, but that larger breeds can utilize to advantage a nutritive ratio of 1 to 2.5. Morgan [61] states that the nutritive ratio of protein to nonprotein foods should be approximately 1 to 2.5 for growing puppies.

McCay [49] observed that the dog digests and absorbs about four-fifths of the protein in the usual mixed feeds. Melnick and Cowgill's [57] studies on the minimum intake of various proteins required to give a positive nitrogen equilibrium were excellently controlled and give us the best minimum quantitative requirements to date. Their ration consisted of Crisco or lard 23 per cent, sucrose 57–64 per cent, bone ash 2.5 per cent, salts 1.8 per cent, protein 8.41–15.4 per cent, and vitamin supplements.

Protein was added at varying levels at the isodynamic expense of carbohydrate. Throughout the test period constant weight of the dogs was maintained on 70 calories per kg. of body weight. They assigned the following relative biological values of different proteins for the dog: lactalbumin 100, serum protein 80, casein 73, gliadin 33. The protein requirement per kilogram of body weight necessary for positive nitrogen balance was as follows: lactalbumin 1.15 g., serum protein 1.5 g., casein 1.6 g., gliadin 3.45 g.

The work of Koehn [37] clearly demonstrates that a diet made up exclusively of vegetable components can satisfy the protein requirement of the dog. In general a diet supplying 20 per cent protein of a good quality is sufficient for the dog under all conditions.

Aside from the numerous observations that certain proteins do not contain sufficient quantities of the essential amino acids, it is also apparent that various proteins may contain toxic compounds. Koehn [37] observed that cottonseed meal was toxic when fed at levels to supply all the protein of the diet. Melnick and Cowgill [57] produced a syndrome in dogs referred to as "Frights Disease" by feeding 16 per cent gliadin. Extensive work done at the Wisconsin laboratory [6[illegible]] points toward the causative agent to be a toxic substance found in bleached wheat gluten.

Thus, it should be remembered that mere expression of the protein content of a diet by N × 6.25 is occasionally very insignificant. The level of protein required for optimum nutrition is dependent upon not only quantity but quality which must be clarified as to: (1) amino acid composition, (2) absence of toxic factors, (3) degree of digestibility, and (4) the effective supplementation of one protein with other proteins.

VITAMIN REQUIREMENTS

Vitamin A. Steenbock et al.,[99] in 1921, reported that young dogs placed on a vitamin A-free diet developed ophthalmia. These results have been repeated and extended by many workers.

Stimson and Hedley [100] and Morgan [61] observed a tendency toward respiratory infection in animals on low or suboptimal vitamin A levels. As also noted in other species, vitamin A deficiency is characterized by the inability to maintain certain epithelial tissues with a resulting keratinization. These changes may present the host more susceptible to invading infectious organisms. The absence of this essential nutrient from the diet over prolonged periods results in xerophthalmia, opacity, ulceration, and sometimes perforation of the cornea. Mellanby [56] found that diets containing a large amount of cereals deficient in vitamin A caused degeneration of the spinal cord and a thickening and enlargement of the bones.

The quantitative requirements for the dog are not well established. This is perhaps due to the great variation in vitamin A storage which is affected by the age, growth, and general nutritional status passed from the bitch to the pup. Crimm and Short [17] concluded that the vitamin A requirement of the dog is between 22 to 47 I.U. per kilogram of body weight. Guilbert et al.[28] correlated the data from a number of species and concluded that 6 to 8 micrograms of vitamin A or 25 to 30 micrograms of beta carotene per kilogram of body weight is sufficient to protect against night blindness.

For maintenance of adult dogs, it is probably safe to conclude that 20 micrograms of vitamin A per kilogram of body weight is sufficient. The carotene requirement has not been adequately studied, although it has been demonstrated that canines can utilize carotene.[12] Under the present status of the determination of the biological activity of carotene, the requirement may be placed at 40 to 60 micrograms per kilogram of body weight per day.

Vitamin D. Although Mellanby [55] in 1921 clearly demonstrated that rickets may be brought about by a deficiency of fat-soluble vitamin in the diet of dogs, there is today a lack of agreement as to the exact vitamin D requirement. The relative proportions and amounts of calcium and phosphorus in the diet are important factors in the etiology of rickets. Koselka, Hart, and Bohstedt [38] stated that collies fed a ration containing 1 per cent $CaCO_3$, 1 per cent $Ca_3(PO_4)_2$, and 5 per cent dried skimmilk as sources of calcium and phosphorus grew normally and were completely protected from rickets when a daily dose of 1 to 1.3 I.U. of vitamin D per kilogram of body weight was fed.

Arnold and Elvehjem [6] showed that normal bone development took place in large dogs (Great Danes) when fed irradiated yeast as a source of vitamin D which supplied 12 I.U. or less daily per kilogram of body weight when the calcium:phosphorus ratio was 1.2:1. As the calcium: phosphorus ratio was increased to 2:1, bone calcification was very poor on this level of vitamin D, but improved as the ratio was reduced.

The composition of dog's milk [4] aids in substantiating the conclusion that the ideal calcium:phosphorus ratio is approximately 1.2 to 1. Hundreds of dogs have been reared in the Wisconsin laboratory on synthetic diets which supply approximately 20 I.U. of vitamin D per kilogram of body weight daily, without encountering any symptoms of rickets.

An overdosage with vitamin D can be more serious than a deficiency of this vitamin. Morgan [61] studied the toxicity of vitamin D in dogs and noted that the feeding of 10,000 units per kilogram of body weight per day resulted in severe calcification of the stomach, heart, lungs, kidneys, and even muscles.

A ration which contains an optimum calcium:phosphorus ratio of approximately 1.2 to 1 should supply approximately 10 to 20 I.U. of vitamin D per kilogram of body weight per day. This amount cannot be supplied by the usual cereal and meat foods employed in formulating diets unless some extra source of vitamin D, such as cod liver oil or irradiated yeast, is added.

Vitamin E. Anderson et al.[2, 3] encountered an acute vitamin E deficiency in dogs fed evaporated mineralized milk diets when undergoing the added strain of gestation and lactation. Pups were often born dead or developed muscle dystrophy about the twentieth day. A lack of muscle tonus, hypersensitivity to pain, and alopecia of the head and limbs were characteristic symptoms. When the dams were given 40 mg. of alpha tocopherol weekly during gestation, normal birth and development of the pups occurred. Twenty-five mg. weekly did not afford protection. The daily requirement of a 6- to 8-kg. dog was approximately 1 mg. of alpha tocopherol per kilogram of body weight. Pups receiving 5 mg. of alpha tocopherol per week grew normally and did not show any signs of deficiency.

Vitamin E is widely distributed in nature and the possibility of occurrence of a vitamin E deficiency is unlikely. However, the vitamin is inactivated by rancid fats, and this fact should be borne in mind.

Vitamin K. A dietary source of vitamin K is not required by the normal dog. Only in such cases where normal bile production is impaired[102] is a prolonged blood clotting time noted, which can be cured by the daily adminstration of 4 mg. vitamin K per kilogram of body weight.

Vitamin C. Dogs are similar to rats in that they do not require preformed sources of ascorbic acid. Hundreds of dogs in many laboratories have been successfully reared on purified diets free of vitamin C. However, the administration of this vitamin may be of therapeutic value in wound healing and numerous infections.

Thiamine. The importance of vitamin B_1 in the diet of dogs has been well established. Karr[34] in 1920 demonstrated with dogs that anorexia is one of the beginning symptoms of thiamine deficiency. The effect of deprivation of this vitamin on appetite is striking.[16] The response to treatment as regards alleviating polyneuritic symptoms and anorexia is perhaps even more striking since cures of the outward symptoms may occur within 12 hours.

The report by Arnold and Elvehjem[7] summarizes the many figures quoted for requirement and further clarified this problem by demonstrating that the thiamine requirement of the dog is dependent upon caloric intake. From these and additional studies[46] one can conclude that the thiamine requirement for growing and mature dogs is amply met with 75 micrograms of thiamine chloride per 100 g. of a fat-low ration. On a high fat diet

(56.5 per cent isocaloric replacement of carbohydrate), the requirement for thiamine is decreased approximately to 28 micrograms per 100 g. of diet.

In general if the diet contains sufficient quantities of untreated whole cereal grains, the animals will receive adequate amounts of this vitamin. Foods subjected to heat and processed products are very likely to be low in thiamine.

Riboflavin. Much information is available as to the essential need for riboflavin in the diet for dogs. The symptoms of riboflavin deficiency and requirements have been described by many workers.[8, 67, 101] As the field of nutrition advances it becomes obvious that much of the early work was complicated by the use of diets which supplied inadequate amounts of other B-complex vitamins. The studies by Potter et al.[67] and Spector et al.[98] give perhaps the more rigid requirement and description of an uncomplicated riboflavin deficiency. From these studies one can predict the requirement to be approximately 100 micrograms per kilogram of body weight for growing weanling pups. Sixty micrograms seems to be sufficient for optimum growth; however, a marked difference in the degree of riboflavin storage on the high and low levels was observed. Axelrod et al.[8] concluded that 100 micrograms per 100 g. of ration was inadequate, whereas 400 micrograms per 100 g. was adequate. Body weight was maintained in adult dogs weighing 10 kg. or more on as little as 15 micrograms per day.[98]

Contrary to the work with rats, the level of fat in the diet seems to have no influence on the requirement.[67] Sarett et al.[77] found that urinary excretion of riboflavin is inversely related to the level of protein intake.

The general symptoms of a deficiency of this vitamin in dogs are clearly described by the experiments of Potter et al.[67] The food intake of control dogs receiving 100 micrograms of riboflavin per kilogram of body weight per day was restricted to that of a paired mate on a deficient diet. The following observations were reported. (1) Fatty livers. The fat content on a moisture-free basis ranged from 42.4 to 55.5 per cent, whereas controls contained 13.1 to 16.5 per cent fat. (2) Anemia. Hemoglobin values varied from 9.9 to 12.3 g. per cent. That normal blood formation depends upon an adequate intake of riboflavin was earlier demonstrated by Sebrell and Onstott.[92] Spector et al.,[98] studying the relation of various B-complex vitamins to hematopoiesis, noted that phlebotomy in the absence of riboflavin produced a microcytic hypochromic anemia. (3) Muscular weakness. A muscular weakness of the hind quarters was observed shortly before the collapse syndrome. (4) Dermatitis. A dry, flaky dermatitis accompanied by a marked erythema on the hind legs, chest, and abdomen was noted. (5) Eye symptoms. A watery discharge from the eyes accompanied by a conjunctivitis appeared in 4 to 9 weeks followed by a vascularization of the cornea and a pulling forward of the nictitating membrane. Opacity of the cornea was noted in 50 per cent of the deficient animals. (6) Heart rate. In general tachycardia was noted a few hours prior to the collapse syndrome.

Niacin. A deficiency syndrome called blacktongue in dogs was found to be similar to the disease called pellagra in humans as early as 1928.[26] One of the great contributions to human nutrition was made possible by the use of the dog as the assay animal in the isolation and identification of niacin as the active compound in the cure and prevention of this deficiency disease.[19] The early studies on the requirement of canines for this vitamin utilized the Goldberger diet which consists chiefly of white corn meal.

The majority of the studies on the optimal requirement for niacin dealt with single curative-dose feedings. Thus, conversion of the requirement under such conditions to the natural minimum level necessary to prevent deficiency symptoms, and yet maintain the optimum nutritional status of the animals, should be done with considerable caution. The single curative dose feeding technique should give values greater than the actual requirement. Sebrell[93] et al. concluded that 20 to 60 mg. of niacin was necessary to cause acute symptoms of blacktongue to subside, and that a 10 mg. semiweekly dose, or approximately 0.5 mg. per kg. of body weight per day, was ample to prevent blacktongue for a period of 6 months. Dann et al.[18] accepted 0.15 mg. per kilogram as the preventive dose. Using a purified diet[82] practically devoid of niacin, the requirement as calculated by single dose feedings, for adult dogs, ranged from 0.20 to 0.23 mg. per kilogram of body weight per day, and for weanling growing puppies ranged from 0.25 to 0.365 mg.

The administration of sufapyridine[41, 82] and sulfathiazole to dogs exhibiting symptoms of blacktongue inhibits the curative effect of niacin. The feeding of fresh liver with sulfapyridine or sulfathiazole corrects blacktongue symptoms and normal growth is resumed. Thus, in practical treatment of blacktongue when localized infections are treated simultaneously with these drugs, the logical therapy would indicate the feeding of fresh liver.

The speed of onset of deficiency symptoms when niacin is omitted from a purified diet seems to vary with the protein content of the ration. Employing 18 per cent casein in the purified diet typical blacktongue symptoms, such as drastic loss in weight, anorexia, inflammation of the gums, and palatine redness appeared in weanling growing puppies in 14 to 18 days and in adult dogs in 30 to 45 days.[82] Morgan[62] employing purified rations containing approximately twice this amount of protein states that "Even in very young animals several months are required for the development of overt symptoms of deficiency in any of the B vitamins with the possible exception of B_1.''

It was observed [80, 82] that occasionally dogs undergoing repeated niacin deficiencies eventually fail to respond to niacin, but recover upon administering liver concentrates. Thus by extending these observations,[39] it was shown that folic acid is required to elicit a greater number of responses to niacin. Ruegamer et al.[76] noted that, even when including biotin and folic acid in the ration of dogs who were on repeated niacin deficiency studies, eventually the animal fails to respond to niacin and shows anorexia, loss of weight, diarrhea, develops a progressive macrocytic anemia, and dies. This deficiency could be corrected by administering daily intramuscular injections of 0.5 cc. of a pernicious anemia liver extract or a few drops of Reticulogen (Lilly).

Krehl et al.[40] reported that when unenriched corn grits are incorporated in a synthetic ration to the extent of 60 per cent of the sucrose (original diets contained 66 per cent sucrose), the niacin requirement of the dog is markedly increased. They concluded that on such diets 3 times as much niacin is required for comparable growth on a purified or whole milk ration. This observation is interesting; however, the description of the experimental procedure (which omits control groups, sex, and litter numbers) is far too meager to warrant the conclusions drawn.

Singal et al.[95] reported that blacktongue symptoms could be cured via administering 0.5 per cent of L- or DL-tryptophan in lieu of niacin and that urinary nicotinic acid fractions were promptly increased.

Pyridoxine. Fouts et al.[21, 22] showed that adult dogs and weanling pups fed a purified diet low in pyridoxine developed a nutritional microcytic hypochromic anemia. These results were confirmed by several laboratories and are discussed in the report by McKibbin et al.[53] Failure to demonstrate a complete remission from the anemia due to this deficiency was observed in several studies.[11, 53] Following the immediate stimulation in blood formation afforded by pyridoxine therapy, the lag in complete remission could be corrected only by the administration of liver extracts or other crude sources of the B complex. It was shown that pantothenic acid, choline, or additional amounts of thiamin, riboflavin, or niacin were not the active factor. This question to date is still unsolved; however, further studies using biotin and folic acid have not been tried.

In the anemia which accompanies a chronic pyridoxine deficiency, the blood plasma iron is abnormally high and drops to a low normal level during the remission.

Sarma et al.[78] noted that pyridoxal, pyridoxamine, and pyridoxine administered intravenously were equally active in promoting growth and hemoglobin regeneration.

Several workers [22, 53] used a level of 60 micrograms of pyridoxine per kilogram of body weight per day for curative therapy; however, information is not available as regards the minimum protective maintenance requirement. Work with other animals indicates that the requirement for pyridoxine closely approximates that of thiamin (20 micrograms per kilogram of body weight).

Pantothenic Acid. McKibbin et al.[51] produced a fatal deficiency in dogs by feeding a purified diet supplemented with thiamine, niacin, riboflavin, and pyridoxine. Deficiencies produced by such rations were remedied by highly purified pantothenic acid concentrates. Later studies [81] using crystalline pantothenic acid and further supplementing the diet with choline confirmed the requirement of the dog for pantothenic acid. A study of the requirement for this vitamin for optimum growth conducted on several litters of weanling pups indicated that approximately 100 micrograms per kilogram of body weight per day are adequate.

This deficiency manifests itself very suddenly, often without the usual outward symptoms of anorexia or acute loss of body weight. The final syndrome prior to death is characterized by sudden prostration, distressing cardia, respiratory, intestinal and skeletal muscular symptoms. Necropsy of the deficient dogs revealed fatty livers (34.7 to 55.1 per cent fat on dry basis), mottled thymuses, hemorrhagic kidney degeneration, gastritis, and intussusceptions. The hypogleemia noted in the severely deficient animals was lowered to a level which could readily have been the cause of the coma. This hypoglycemia is of interest in connection with the severe fatty degeneration of the liver which indicates the absence of liver glycogen. Considering that the diet in these studies contained 66 per cent sucrose, it may suggest a fundamental impairment of carbohydrate metabolism. Blood chlorides were also lowered and nonprotein nitrogen values raised.

The intravenous administration of pantothenic acid to animals in a comatose state usually failed to bring about a response; however, when glucose, saline, and pantothenic acid were injected simultaneously, a dramatic remission from the coma and subsequent complete recovery occurred.

Choline. The importance of choline in the metabolism of fat was discovered by Best et al.[10] through work with depancreatized dogs. Using a purified diet [79] containing 18 per cent casein and 11 per cent fat, it was shown that young weanling pups required choline for normal growth. The dog is similar to the rat in that many factors influence the choline requirement such as the protein, methionine, and fat levels of the diet. On an 18 per cent extracted casein diet failure was very rapid (2 to 3 weeks) in the majority of the pups; however many survived this critical period and grew normally. McKibbin et al.[54] conducted extensive studies on choline deficiency in dogs, utilizing a semipurified peanut meal-casein-sucrose diet. They concluded that the choline requirement for the growing pup on such a ration is probably not more than 100 mg. per 100 g. of ration or 50 mg. per kilogram of body weight per day.

A fatal choline deficiency was produced in less than three weeks. The deficiency was characterized by a severe fatty infiltration of the liver, rise in blood plasma phosphatase, impairment in bromsulfalein elimination, and a fall in blood plasma cholesterol and cholesterol esters. In a severe deficiency there was in addition an increase in prothrombin time and a decrease in blood hemoglobin, hematocrit, and plasma proteins.

Seven-tenths per cent DL-methionine supplemented to the ration apparently afforded complete protection. It is interesting to note that with the diets they employed it was necessary to add a liver concentrate to obtain normal growth. The authors suggested that this requirement for another B-complex vitamin could be the eluate factor required by chicks (recently shown to be folic acid).

Other B-Complex Vitamins. Hundreds of dogs have been reared on a purified diet of 19 per cent casein, 66 per cent sucrose, 11 per cent fat, 4 per cent salt mixture, supplemented with vitamins A, D, thiamine, pyridoxine, niacin, riboflavin, pantothenic acid, and choline.[52]

By further purifying the casein used in the early studies, by repeated alcohol extraction, it was shown that pups receiving the above purified ration occasionally grew erratically and sub-optimally.[80] In these animals, growth could be increased by the addition of liver extract to the ration. *p*-Aminobenzoic acid and inositol did not replace the liver extract.

The inclusion of 0.5 per cent to 4 per cent succinylsulfathiazole in such a diet in an attempt to suppress possible intestinal synthesis produced no signs of another deficiency. Subjecting dogs to severe phlebotomy while receiving these purified diets did not alter their ability to regenerate a nomal bloodstream.[59]

Seeler and Silber[94] reported that dogs were maintained in apparent good health for 4½ years on a purified diet (30 per cent casein), supplemented only with thiamine, riboflavin, niacin, pyridoxine, and pantothenic acid.

Reports by other laboratories[42, 97] indicate that additional factors supplied by yeast or liver are necessary for optimum growth. These workers fed high fat, low choline diets. Ruegamer et al.[74] employing high fat, high choline diets found that dogs grow well and maintain a good state of health without receiving any B-vitamins in addition to the six mentioned. However, by feeding a highly purified alcohol extracted casein, it was observed that hemoglobin levels plateau at 11 to 14 g. per cent and achromotrichia often developed. They presented preliminary evidence which points toward the possible role of biotin in producing hemoglobin levels of 16 to 16.5 g. per cent. The claim by Smith[97] for the essential requirement of biotin to prevent a specific paralysis syndrome in dogs was not substantiated by the studies of Ruegamer et al.[73] When a diet identical to that described by Smith was fed to growing dogs, the animals failed to grow and developed a paralysis which was curable with potassium.

The nutritional requirement of the dog subjected to repeated niacin deficiencies and cures deviates from the normal. Thus the essential need for folic acid[39] and a factor supplied by anti-pernicious anemia liver extracts[76] was established. The role of folic acid in the nutrition of the dog placed on fat-free diet[72] further emphasizes the fact that, when an abnormal diet or abnormal physiological condition exists, our present knowledge of dog nutrition may be quite incomplete.

The studies of McKibbin et al.,[54] using extracted peanut meal as a component of a purified diet, revealed that in order to obtain normal growth in pups it was necessary to supplement the dietary with a liver extract. Thus it is obvious that variations in the foods used in formulating a dietary may considerably alter the nutritional requirements of the animal. This emphasizes another approach for the researchers interested in both academic and practical aspects of the nutritional requirements of the dog.

The danger of imbalance of niacin, pantothenic acid, and unknown factors by administering large amounts of certain B vitamins is emphasized by Morgan.[62]

Thus far the many experiments on the basic nutritional requirements of dogs have dealt mainly with growth and maintenance for short periods. As long-term experiments are conducted especially in relation to reproduction, the list of required dietary essentials may be extended.

Mineral Requirements

Relatively little is known about the minimum quantitative requirements for the minerals. Eleven elements—calcium, phosphorus, sodium, chlorine, potassium, iron, copper, iodine, magnesium, manganese, and zinc—are considered essential and indications place cobalt in the probable category.

As previously mentioned, the ratio of calcium and phosphorus is of great importance. The ratio of 1.2:1 seems to be most favorable. As Morgan[60] pointed out, an excess of calcium increases the demand for vitamin D and most rickets observed in dogs is of the low phosphorus type.

Dog foods containing appreciable quantities of plant products must have salt added. Since plant sources are high in potassium and low in sodium, this effect must be counterbalanced. The requirement of the dog for potassium and the syndrome resulting when the diet is deficient in this element were clearly demonstrated by Ruegamer et al.[73]

Numerous studies have been made on the requirement of iron and copper in hemoglobin regeneration after hemorrhage [24, 52] and in the cure of a nutritional anemia produced by feeding a whole milk diet.[68] Frost et al.[24] calculated that a milk diet supplies less than 0.1 to 0.2 mg. of iron per kilogram of body weight per day. Thus this level is inadequate since anemia develops consistently on unmineralized milk diets. A minimum level of 0.6 mg. of iron per kilogram of body weight was found to give optimal hemoglobin response.[68] The iron in wheat bran is 100 per cent available whereas the iron in spinach is only 20–40 per cent available. Since 0.6 mg. of iron per kilogram of body weight supports optimum hemoglobin regeneration after anemia is apparent, the requirement for maintenance would be less than this level.

TABLE 119. FOOD MAINTENANCE REQUIREMENTS OF MATURE DOGS [6]

Body Weight kg.	Grams Dry Food per Animal	Calories per kg.	Grams Food per Animal Fresh Basis 70% Moisture
1	35.3	141.0	118
2	58.5	117.0	195
3	78.7	105.0	262
4	97.0	97.0	323
5	114.0	91.0	380
6	130.0	86.7	433
7	146.0	83.6	487
8	161.0	80.6	537
9	175.0	77.8	583
10	189.0	75.5	630
20	313.0	62.5	1040
30	423.0	56.3	1410
40	523.0	52.3	1740
50	613.0	49.0	2043

The requirement of copper has been suggested as roughly being 1/10 that of iron.[52] The need for cobalt in hematopoiesis has been proposed by many workers. Frost et al.[25] stated that a cobalt deficiency as evidenced by hematopoietic responses to cobalt at a minimum level of 0.1 mg. per day occurred in about 50 per cent of the dogs studied. Cobalt has a toxic effect which results in polycythemia when fed at levels of 2 mg. per kilogram of body weight. Also, when cobalt is administered at this level prior to the feeding of iron or copper, an inhibition to blood regeneration occurs. This inhibition of hemoglobin formation after both iron and copper are fed is rapidly overcome by feeding various liver extracts. Extensive studies on this problem revealed that when a milk diet containing iron, copper, manganese, and cobalt was supplemented with synthetic B vitamins, cystine, uropterin concentrates, and bile salts, blood regeneration comparable to that produced by liver preparations occurred.

Extensive studies on dogs fed purified diets containing 4 per cent of "Phillips and Hart"[66] salt mixture have proved that the mineral requirements for the growing dog are satisfied.

In practical dog rations the minerals most likely to be low are calcium, phosphorus and salt. In general, the other essential mineral elements are needed in relatively small amounts and are usually contained in sufficient quantities in natural foods. The greatest need for mineral supplementation is in pups reared away from the bitch on a simulated milk formula.

TABLE 120. APPROXIMATE PROTEIN AND VITAMIN REQUIREMENTS OF DOGS

	Growth		Maintenance	
	Per kg. Body Weight per Day	Per 100 g. of Dry Ration	Per kg. Body Weight per Day	Per 100 g. of Dry Ration
Protein, g.	2.5 to 5.0	20	1.0 to 1.5	12 to 20
Vitamin A, micrograms	20	80	10	40
Vitamin D, I.U.[1]	20	80	10	40
Thiamine, micrograms	20 to 30	75	10 to 20	50
Riboflavin, micrograms	60 to 100	400	25	200
Niacin, micrograms	300 to 400	1000	200 to 250	500
Pyridoxine, micrograms	20 to 30	75	10 to 20	50
Choline, mg.	50	100	30	75

[1] I. U.—International Unit.

A summary of the approximate nutritional requirements of the dog is given in Tables 119, 120, and 121.

FUR-BEARING ANIMALS

The factual knowledge on the nutritive requirements of fur-bearing animals is very limited. The main fur animals that are raised commercially are foxes and minks; thus this discussion is confined to these species. Studies on the nutritive requirements of the fox have progressed more than for mink.

Since foxes and minks are carnivores, fur farmers have utilized horsemeat or fish as the main component of the ration for these animals. A survey conducted by Coombes[14] in 1939 to determine the composition of mink rations fed by 28 major fur farmers throughout Wisconsin revealed that about 70 constituents were utilized in 28 different formulas. In general, the average fox or mink ration is composed of 60 to 75 per cent meat (usually horsemeat), 5 to 10 per cent fresh liver, 10 to 30 per cent cereal mixture, and 5 to 10 per cent vegetables. The practical and economic aspect of feeding thousands of animals such a ration is obvious. The goal desired would be a dry ration, low or void in meat, which could be stored without refrigeration. That these carnivorous animals would consume a dry, meatless diet was looked upon with much skepticism by fur farmers. Recent research[86, 87] has indicated that purified rations similar to those employed in studying the nutritional requirements of the dog are vigorously consumed by foxes and minks. This observation affords a tool by which the fundamental nutritional requirements of these species can be determined with more certainty and rapidity than by the use of practical diets.

TABLE 121. MINERAL REQUIREMENTS OF DOGS

	Arnold and Elvehjem Values[8]	Estimated Approximate Requirement
Mineral	Mg./Kg. of Body Weight per Day	Mg./100 g. of Dry Ration
Ca	20.000	180.00
P	40.000	150.00
NaCl	300.000	1,200.00
K	80.000	300.00
Mg	10.000	40.00
Fe	0.400	2.00
Cu	0.060	0.20
Mn	0.040	0.15
Zn	0.060	0.15
I	0.001	0.01

Energy Requirement. Palmer[65] was one of the earliest workers to use foxes and minks in nutritional studies, and was mainly interested in their caloric requirement. The results he obtained were substantiated by Hodson and Smith[32] who have shown that the caloric requirements for maintenance of foxes and minks are approximately equal when expressed in terms of calories per square meter of body surface (2102 for foxes, 2370 for minks). However, when calculated as calories per kilogram of body weight, foxes require 120 and minks 273 calories. It must be remembered that the above figures are for maintenance only; thus the growing, pregnant, and lactating animal would require more calories per unit of body weight or body surface.

Protein Requirements. Optimum protein requirements have not been established, although Smith[96] recommends 30 to 68 g. of protein per day for foxes depending upon the size of the animal and period of the year. Employing purified rations[55] it was found that weanling foxes and minks gained in body weight as rapidly on 19 per cent casein as on 30 per cent casein. McDermid and Ott[50] have emphasized that a high protein diet is the underlying cause producing the disturbance in mink called "yellow fat." A starvation technique was recommended to prevent this condition. No reference is made by the authors as to the percentage of protein considered as too high. This is a dangerous general acquisition and must be thoroughly investigated prior to making drastic alterations in the diet.

Vitamin Requirements. *Vitamin A.* The requirement and utilization of vitamin A and carotene by foxes have been reviewed and further investigated by Bassett et al.[9] A deficiency of vitamin A or carotene is characterized by head cocking, whirling, unsteady gait, lethargy, eye troubles, urinary calculi, and poor quality fur. These workers recommend that growing pups be fed between 100 to 600 I.U. (23.2 to 138.2 micrograms) of vitamin A, or at least 600 I.U. (360 micrograms) of carotene per kilogram of body weight.

Vitamin D. Early observations by Hanson[30] on the occurrence of nutritional deficiencies in foxes dealt with the incidence of rickets. Allen[1] reviewed the high mortality in mink due to rickets which in 1932 caused a loss of 80 per cent of the mink crop in Manitoba. Rickets is produced in these species not only by a deficiency of vitamin D, but also by a low calcium, a high phosphorus, or improper Ca:P ratio diets. Ott and Coombes[64] produced rachitic symptoms in fox pups by employing a ration low in vitamin D with a Ca : P ratio of 7 :1. Harris et al.[31] observed rickets in growing fox pups receiving a ration containing 0.52 per cent phosphorus and 0.16 to 0.41 per cent calcium (on a dry basis) along with 1.29 per cent cod liver oil. They concluded that 0.51 per cent calcium, when the ration contains 0.52 per cent phosphorus, was the minimum requirement to prevent rickets and insure proper growth.

Vitamins E, K, and C. The requirement of foxes and minks for vitamin E has not been studied. Both species have been reared and maintained for limited periods on purified diets free of vitamin K and ascorbic acid. The addition of either or both of these vitamins did not exert any beneficial effect. In this relationship foxes and minks are similar to dogs and rats in that a preformed dietary source of these two vitamins is not essential.

Thiamine. The occurrence of Chastek paralysis in foxes stimulated studies on the nutritional requirements of this species. Green et al.[27] and Coombes[15] revealed that this disease was fundamentally a B_1 avitaminosis which was brought about by the inclusion in the ration of 10 per cent or more of certain fresh or frozen fish such as carp, suckers, Atlantic whiting, and quill backs. Woolley [103] indicated that the causative agent was an enzyme in raw fish which destroys thiamine. It is now well established that cooking the fish prior to mixing into the ration destroys this harmful property. Raw fish may be fed with safety if nutritionally adequate rations (free of fish) are fed on alternate days.

Ender and Helgebostad [20] determined the minimum thiamine requirement for fox pups to be about 100 micrograms per day, and for lactating females to be about ten times this amount.

Riboflavin, Niacin, Pantothenic Acid, and Pyridoxine. By employing purified rations it was clearly established that weanling fox pups require riboflavin, pantothenic acid, niacin, and pyridoxine.[89] The deficiency symptoms when one of the above vitamins is omitted from the ration closely resemble those reported in similar studies with dogs. The rapidity with which the deficiencies develop, especially of riboflavin, pantothenic acid, or niacin, is often 2 to 4 weeks after the animal is placed on experiment. The minimum and optimum requirements of these vitamins have not been determined; however, preliminary evidence indicates a close correlation with the requirements of dogs (with the exception of niacin which seems considerably higher for foxes).

Folic Acid. Adult and young mink [85, 86] and foxes [87] fed purified diets containing varying levels of protein, supplemented with thiamine, riboflavin, pantothenic acid, niacin, and choline develop critical deficiency symptoms which can be cured or prevented by the administration of crystalline folic acid. Deficiency symptoms are characterized by irritability, weakness, anemia, severe loss in body weight, bloody diarrhea, and fatty livers. Autopsy of mink allowed to die of this deficiency revealed ulcerative hemorrhagic gastritis localized mainly in the stomach and small intestines.

The optimum requirements have not been established. However, curative therapy in mink was attained with 50 micrograms per day and in foxes with 25 micrograms per 100 g. of ration. Recent investigations [83] indicate that a diet supplying 25 micrograms per 100 g. is sufficient for growth and maintenance of foxes and minks. This requirement may be considerably higher during pregnancy and lactation.

It is interesting to note that folic acid conjugate (hepta glutamate), as present in yeast, is not utilized when fed to severely folic acid-deficient foxes at levels corresponding to synthetic folic acid (pteroyl glutamic acid), which produced a rapid remission of symptoms.[87] This does not preclude that normal foxes are unable to utilize folic acid conjugate.

Unidentified Factors. Foxes and minks are unable to survive upon a purified diet containing sucrose, casein, mineral salts, cottonseed oil, cod liver oil, and all the known crystalline vitamins.[84] The deficiency is characterized by anorexia, loss in body weight; sub-optimal hemoglobin levels; depigmented, poorly developed fur; paralysis of the hind quarters; very fatty, light colored, enlarged livers; and degenerate kidneys. The feeding of fresh liver or whole raw milk alleviates the deficiency syndrome. Preliminary studies [84, 85, 90] on the fractionation of the unidentified factors in liver indicate that methanol extraction removes one factor and that the methanol-insoluble residue contains another factor.

Kennedy [36] observed numerous outbreaks of a nutritional anemia in minks which he described as follows: "The symptoms of the disease seem to be recognized under the somewhat loose and ambiguous terms acidosis, and sheath trouble. The term sheath trouble is descriptive of one of the common symptoms of anemia in the advanced stages of the disease. A degree of anemia may exist without sheath trouble being apparent, and the term is not applicable to the female." This disease was produced experimentally by the Canadian workers by feeding a ration consisting of 60 per cent horsemeat or fish, 25 per cent cereals, 10 per cent bonemeal, 5 per cent vegetables and small quantities of milk, wheat germ and yeast. The addition of 14 g. of fresh liver to the daily ration prevented the disease.

A comparison of the observations of Kennedy with studies using experimental rations indicates that folic acid and the unidentified liver factors may be the underlying causes for this nutritional disease.

The important role of fresh liver or milk in fox and mink nutrition is a challenge to future research. The requirement of these species for folic acid and still unidentified nutrients emphasizes that taxonomically related species, such as the dog and fox, differ markedly in that what may be considered as a nutritionally adequate diet for one species may be inadequate for another.

SUMMARY

Until the entire story on the nutritional requirements of foxes and minks is unfolded, it is necessary to advance drastic ration changes with caution. In general, one can use as a basic start the information now available for these species, supplemented with the data on the nutritive requirements of the dog. It is undoubtedly safe to conclude that the mineral requirements of fur-bearing animals are adequately met by the levels suggested in Table 121.

As other practical sources of the unidentified liver factors are found, the formulation of practical diets can be made with greater certainty. Among the products showing promise are liver powders (specially prepared so as not to destroy the active nutrients), fish solubles, and whey concentrates. During the past year, numerous fur ranches have successfully reared weanling mink kits and maintained adults on dry, unrefrigerated diets. Their complete success, which would revolutionize the feeding of fur animals, is dependent upon carrying the animals through reproduction.

BIBLIOGRAPHY

1. Allen, J. A., "The Principles of Mink Ranching." Game & Fisheries Branch, Manitoba, Canada (1940).
2. Anderson, H. D., Elvehjem, C. A., and Gonce, J. E., Jr., *Proc. Soc. Expt. Biol. Med.* **42**: 750 (1939).
3. Anderson, H. D., Elvehjem, C. A., and Gonce, J. E., Jr., *J. Nutrition* **20**: 433 (1940).
4. Anderson, H. D., Johnson, B. C., and Arnold, A., *Am. J. Physiol.* **129**: 631 (1940).
5. Arnold, A., and Elvehjem, C. A., *J. A.V.M.A.* **91**: 515 (1937).
6. Arnold, A., and Elvehjem, C. A., *J. A.V.M.A.* **95**: 187 (1939).
7. Arnold, A., and Elvehjem, C. A., *Am. J. Physiol.* **126**: 289 (1939).
8. Axelrod, A. E., Lipton, M. A., and Elvehjem, C. A., *Am. J. Physiol.* **133**: 555 (1941).
9. Bassett, C. F., Harris, L. E., and Wilke, C. F., *Cornell Vet.* **36**: 5 (1946).
10. Best, C. H., Ferguson, G. C., and Hershey, J. M., *J. Physiol.* **79**: 94 (1933).
11. Borson, H. J., and Mettier, S. R., *Proc. Soc. Expt. Biol. Med.* **43**: 429 (1940).
12. Bradfield, D., and Smith, M. C., *Am. J. Physiol.* **124**: 168 (1938).
13. Brody, S., Procter, R. C., and Ashworth, U. S., *Univ. Missouri Res. Bull.* **220** (1934).
14. Coombes, A. I., Unpublished data, Madison, Wis., Univ. Wis. (1939).
15. Coombes, A. I., *Am. Natl. Fur & Mkt. J.* **20**: 13 (1941).
16. Cowgill, G. R., *Am. J. Physiol.* **57**: 433 (1921).
17. Crimm, P. D., and Short, D. M., *Am. J. Physiol.* **118**: 477 (1937).
18. Dann, W. J., Kohn, H. I., and Handler, P., *J. Nutrition* **20**: 477 (1940).
19. Elvehjem, C. A., Madden, R. J., Strong, F. M., and Woolley, D. W., *J. Biol. Chem.* **123**: 137 (1938).
20. Ender, F., and Helgebostad, *Norsk Vet. Tidsskrift, Nr.* **1**: 3 (1943).
21. Fouts, P. J., Helmer, O. M., and Lepkovsky, S., *Proc. Soc. Expt. Biol. Med.* **40**: 4 (1939).
22. Fouts, P. J., Helmer, O. M., and Lepkovsky, S., *Am. J. Med. Sc.* **199**: 163 (1940).
23. Frohring, W. O., *Vet. Med.* **32**: 76 (1937).
24. Frost, D. V., Elvehjem, C. A., Hart, E. B., *J. Nutrition* **19**: 311 (1940).
25. Frost, D. V., Spitzer, E. H., Elvehjem, C. A., and Hart, E. B., *Am. J. Physiol.* **134**: 746 (1941).
26. Goldberger, J., and Wheeler, G. A., *U. S. Pub. Health Rept.* **43**: 172 (1928).
27. Green, R. G., Carlson, W. E., and Evans, C. A., *J. Nutrition* **21**: 243 (1941).
28. Guilbert, H. R., Miller, R. F., and Hughes, E. H., *J. Nutrition* **13**: 543 (1937).
29. Handelsman, M. B., Golden, L. A., and Pratt, J. H., *J. Nutrition* **8**: 479 (1934).
30. Hanson, K. B., *Am. Fur Breeder* **8**: 13 (1935).
31. Harris, L. E., Bassett, C. F., Smith, S. E., and Yoeman, E. D., *Cornell Vet.* **35**: 9 (1945).
32. Hodson, A. Z., and Smith, S. E., *Am. Fur Breeder* **18**: 44 (1945).
33. Ivy, A. C., *No. Am. Vet.* **17**: 44 (1936).
34. Karr, W. G., *J. Biol. Chem.* **44**: 255 (1920).
35. Kaufmann, M., *Arch. ges. Physiol.* **109**: 440 (1905).

36. Kennedy, A. H., *Canadian Silver Fox & Fur* **12**: 13 (1946).
37. Koehn, C. J., *Alabama Polytechnic Inst., Agr. Expt. Sta. Bull.* **251** (1942).
38. Koselka, F. L., Hart, E. B., and Bohstedt, G., *J. Biol. Chem.* **100**: 715 (1933).
39. Krehl, W. A., and Elvehjem, C. A., *J. Biol. Chem.* **158**: 173 (1945).
40. Krehl, W. A., Teply, L. J., and Elvehjem, C. A., *Proc. Soc. Expt. Biol. Med.* **58**: 334 (1945).
41. Krehl, W. A., Torbet, N., de la Huerga, J., and Elvehjem, C. A., *Arch Biochem.* **11**: 363 (1946).
42. Lamboy, J. P., and Nasset, E. S., *J. Nutrition* **26**: 293 (1943).
43. Lewis, H. B., *Biological Symposia* **5**: 20 (1941), Lancaster, Pa., The Science Press Printing Co.
44. Linton, R. G., *Vet. Med.* **32**: 86 (1937).
45. Lössl, H., *Zeit. Hundeforschung* **1**: 69 (1931).
46. Maass, A. R., Michaud, L., Spector, H., Elvehjem, C. A., and Hart, E. B., *Arch. Biochem.* **4**: 105 (1944).
47. Madden, S. C., Carter, J. R., Kattus, A. A., Miller, L. L., and Whipple, G. H., *J. Expt. Med.* **77**: 277 (1943).
48. Magendie, F., *C. R. Acad. Sci.* **13**: 237 (1841).
49. McCay, C. M., "Nutrition of the Dog." Ithaca, New York, Comstock Publishing Co., Inc. (1944).
50. McDermid, A. M., and Ott, G. L., *Am. Fur Breeder* **19**: 32 (1947).
51. McKibbin, J. M., Madden, R. J., Black, S., and Elvehjem, C. A., *Am. J. Physiol.* **128**: 102 (1939).
52. McKibbin, J. M., Schaefer, A. E., Elvehjem, C. A., and Hart, E. B., *J. Biol. Chem.* **145**: 107 (1942).
53. McKibbin, J. M., Schaefer, A. E., Frost, D. V., and Elvehjem, C. A., *J. Biol. Chem.* **142**: 77 (1942).
54. McKibbin, J. M., Thayer, S., and Stare, F. J., *J. Lab. & Clin. Med.* **29**: 1109 (1944).
55. Mellanby, E., *Med. Res. Counc. Spec. Rept. Ser. No.* **61**, 1921.
56. Mellanby, E., *J. Physiol.* **99**: 467 (1941).
57. Melnick, D, and Cowgill, G. R., *J. Nutrition* **14**: 401 (1937).
58. Michaud, L., and Elvehjem, C. A., *No. Am. Vet.* **25**: 657 (1944).
59. Michaud, L., Maass, A. R., Ruegamer, W. R., and Elvehjem, C. A., *Proc. Soc. Expt. Biol. Med.* **56**: 148 (1944).
60. Morgan, A. F., *No. Am. Vet.* **15**: 24 (1934).
61. Morgan, A. F., *No. Am. Vet.* **21**: 476 (1940).
62. Morgan, A. F., *Science* **93**: 261 (1941).
63. Newell, G. W., and Elvehjem, C. A., Unpublished data (1947).
64. Ott, G. L., and Coombes, A. I., *Vet. Med.* **36**: 202 (1941).
65. Palmer, L. S., *Am. Fox & Fur Farmer* **7**: 22 (1927).
66. Phillips, P. H., and Hart, E. B., *J. Biol. Chem.* **109**: 657 (1935).
67. Potter, R. L., Axelrod, A. E., and Elvehjem, C. A., *J. Nutrition* **24**: 449 (1942).
68. Potter, V. R., Elvehjem, C. A., and Hart, E. B., *J. Biol. Chem.* **126**: 155 (1938).
69. Rose, W. C., and Rice, E. E., *Science* **90**: 186 (1939).
70. Roseboom, B. B., and Patton, J. W., *J. A.V.M.A.* **74**: 768 (1929).
71. Roseboom, B. B., and Patton, J. W., *Am. J. Physiol.* **100**: 179 (1932).
72. Ruegamer, W. R., and Elvehjem, C. A., Unpublished data (1947).
73. Ruegamer, W. R., Elvehjem, C. A., and Hart, E. B., *Proc. Soc. Expt. Biol. Med.* **61**: 234 (1946).

74. Ruegamer, W. R., Michaud, L., Elvehjem, C. A., and Hart, E. B., *Am. J. Physiol.* **145**: 23 (1945).
75. Ruegamer, W. R., Michaud, L., Hart, E. B., and Elvehjem, C. A., *J. Nutrition* **32**: 101 (1946).
76. Ruegamer, W. R., Torbet, N., and Elvehjem, C. A., *Fed. Proc.* **6**: 286 (1947).
77. Sarett, H. P., Klein, J. R., and Perlzweig, W. A., *J. Nutrition* **24**: 295 (1942).
78. Sarma, P. S., Snell, E. E., and Elvehjem, C. A., *Proc. Soc. Expt. Biol. Med.* **63**: 284 (1946).
79. Schaefer, A. E., McKibbin, J. M., and Elvehjem, C. A., *Proc. Soc. Expt. Biol. Med.* **47**: 365 (1941).
80. Schaefer, A. E., McKibbin, J. M., and Elvehjem, C. A., *J. Nutrition* **23**: 491 (1942).
81. Schaefer, A. E., McKibbin, J. M., and Elvehjem, C. A., *J. Biol. Chem.* **143**: 321 (1942).
82. Schaefer, A. E., McKibbin, J. M., and Elvehjem, C. A., *J. Biol. Chem.* **144**: 679 (1942).
83. Schaefer, A. E., Tove, S. B., Elvehjem, C. A., Unpublished data, 1947.
84. Schaefer, A. E., Tove, S. B., Whitehair, C. K., and Elvehjem, C. A., *Zeit. Vitaminforschung* **19**: 12 (1947).
85. Schaefer, A. E., Tove, S. B., Whitehair, C. K., and Elvehjem, C. A., *J. Nutrition* **35**: 157 (1948).
86. Schaefer, A. E., Whitehair, C. K., and Elvehjem, C. A., *Proc. Soc. Expt. Biol. Med.* **62**: 169 (1946).
87. Schaefer, A. E., Whitehair, C. K., and Elvehjem, C. A., *Arch. Biochem.* **12**: 349 (1947).
88. Schaefer, A. E., Whitehair, C. K., and Elvehjem, C. A., *Am. Natl. Fur & Mkt. J.* **26**: 13 (1947).
89. Schaefer, A. E., Whitehair, C. K., and Elvehjem, C. A., *J. Nutrition* **34**: 131 (1947).
90. Schaefer, A. E., Whitehair, C. K., and Elvehjem, C. A., *J. Nutrition* **35**: 147 (1948).
91. Scudi, J. V., and Hamlin, M., *J. Nutrition* **24**: 273 (1942).
92. Sebrell, W. H., and Onstott, R. H., *U. S. Pub. Health Rept.* **53**: 83 (1938).
93. Sebrell, W. H., Onstott, R. H., Fraser, H. F., and Daft, F. S., *J. Nutrition* **16**: 355 (1938).
94. Seeler, A. O., and Silber, R. H., *J. Nutrition* **30**: 111 (1945).
95. Singal, S. A., Sydenstricker, V. P., and Littlejohn, J., *Fed. Proc.* **6**: 422 (1947).
96. Smith, S. E., *Arch. Biochem.* **1**: 263 (1942).
97. Smith, S. G., *Am. J. Physiol.* **144**: 175 (1945).
98. Spector, H., Maass, A. R., Michaud, L., Elvehjem, C. A., and Hart, E. B., *J. Biol. Chem.* **150**: 75 (1943).
99. Steenbock, H., Nelson, E. M., and Hart, E. B., *Am. J. Physiol.* **58**: 14 (1921).
100. Stimson, A. M., and Hedley, O. F., *U. S. Pub. Health Rept.* **48**: 445 (1933).
101. Street, H. R., and Cowgill, G. R., *Am. J. Physiol.* **125**: 323 (1939).
102. Thaddea, S., *Z. Physiol. Chem.* **279**: 94 (1943).
103. Woolley, D. W., *J. Biol. Chem.* **141**: 997 (1941).

PART IV

PESTICIDES

Chapter XX

INSECTICIDES

DONALD E. H. FREAR

The Pennsylvania State College, State College, Pa.

The control of insect pests affecting agricultural crops, domestic animals, and man has been of considerable economic importance to mankind since the beginning of civilization. Although there are a number of ways in which insect populations may be reduced, such as mechanical methods (hand picking, traps, etc.), biological methods (birds, reptiles, and parasitic organisms), as well as by certain environmental adjustments, the method most commonly practiced involves the use of chemical substances to kill or repel the pests concerned.

Materials which kill insects are commonly called insecticides, and substances which discourage the attacks of insects are designated as repellents or insectifuges. A further classification may be made on the basis of the method by which insecticides act: those which kill by direct action on the organism are designated as *contact insecticides,* and those which act internally after ingestion by the insect are termed *stomach poisons.* Insecticides which act in the gaseous state are called *fumigants.*

Each of these classes of insecticides is of importance in the general scheme of insect control. For some insects which chew the leaves, flowers, or stems of plants, a stomach poison is usually effective. For insects which attack man or animals, or which suck the sap of plants, contact insecticides are most frequently used. In stored products, or for insects infesting houses, ships, warehouses, and similar structures, fumigants are usually employed.

Insecticides may be applied in a number of ways, the best method to be used being determined by the nature of each individual problem. When dissolved or suspended in water or other liquid, application is made as a finely-divided *spray.* This method is probably more frequently used than any other. Water as a diluent is low in cost, and is usually readily available. Organic solvents, such as the hydrocarbon oils, are frequently used in household sprays, and emulsions of two immiscible liquids are used commonly on certain agricultural crops. *Dusts* are prepared by diluting the toxicant with a finely-divided solid, and are applied by suitable mechanical means, usually with the aid of a blast of air. Dusts have the advantage of light weight as compared to sprays, but in most cases the dust deposits do not adhere as well as spray deposits.

Fumigants may be applied in the form of solid, liquid, or gas, but in order to be efficient they must be readily volatile. Most fumigants are applied to spaces which are capable of being tightly closed. *Aerosols* are finely divided solids or liquids, the individual particles being of colloidal dimensions, so that they partake of many of the properties of gases. Aerosols are usually generated by the rapid expansion of an inert gas under pressure.

By the proper choice of insecticide and application method it is possible to control practically all insects. The nature of the insect to be destroyed, its feeding and breeding habits, as well as its location, all must be considered in choosing the proper insecticide. In the discussion to follow, no attempt will be made to recommend specific materials. Rather, the chemical, physical, and biological properties of the more commonly used insecticides will be discussed.

Inorganic Insecticides

The Arsenicals. The highly poisonous nature of the element arsenic and its compounds early suggested their use as insecticides, and it is probable that arsenic preparations were among the earliest known pest-killing substances. Compounds of arsenic are still widely used for this purpose, and in general are highly efficient insecticides. They have the decided disadvantage, however, of being highly toxic to all forms of life, and for this reason they must be used with caution, particularly on food crops.

Arsenic Oxides. Two oxides of arsenic are known: arsenious oxide, As_4O_6 (also known as arsenic trioxide, and frequently written As_2O_3), and arsenic oxide, As_2O_5 (sometimes called arsenic pentoxide or arsenic acid). Arsenious oxide is a by-product of the roasting of mineral ores, and when pure is a white solid which sublimes at 125–150° C. When reacted with alkalies, a series of arsenites is formed. Arsenious oxide is used for insecticidal purposes only in the formulation of certain poison baits, since it is highly toxic to plant as well as animal life.

Arsenic pentoxide is formed by the oxidation of arsenious oxide, and combines with alkalies to form the very important series of salts called the *arsenates*. Of these, the *orthoarsenates* are of considerable importance as insecticides.

Calcium Arsenates. When calcium hydroxide is allowed to react with arsenic pentoxide in solution, several calcium arsenates are possible. For some time it was considered that the main products of this reaction were $CaHAsO_4$, or $Ca_3(AsO_4)_2$,[12] but it has been found that under present commercial manufacturing procedures the basic calcium arsenates predominate. The most common of these has the formula $[Ca_3(AsO_4)_2]_3 \cdot Ca(OH)_2$. Commercial preparations of calcium arsenate quite probably are mixtures of all three of these compounds.[30, 32]

Calcium arsenate is decomposed rather readily when exposed after application to plant surfaces. The reaction is apparently one of hydrolysis and the main products of reaction are $Ca(OH)_2$ and H_3AsO_4. The latter is highly phytotoxic, and may cause severe injury to growing plants.[29] To counteract this, an excess of calcium hydroxide is usually applied with calcium arsenate. The hydrolytic reaction is thus retarded, and less plant injury results. In time, however, the calcium hydroxide becomes carbonated by atmospheric carbon dioxide, and the decomposition of the calcium arsenate proceeds. Calcium arsenate is used as a stomach poison, and has found its principal use on plants such as cotton and potatoes which are not highly susceptible to arsenic injury.

Lead Arsenates. When arsenic pentoxide in solution is allowed to react with litharge, the main product of the reaction is acid lead arsenate, $PbHAsO_4$. This is the material commonly called "lead arsenate" in commerce. It is possible to vary the conditions of reactions, however, so that basic lead arsenates may be produced.[23] These have special uses, and will be discussed later.

Acid lead arsenate as commercially produced is a finely divided solid, with a specific gravity of approximately 6.0. It is very sparingly soluble in water, and does not decompose as readily as calcium arsenate. For this reason it is considered safer to use on plants. When applied with other pest control chemicals such as lime sulfur solution, double decomposition takes place rather readily, probably according to the reaction.

$$2PbHAsO_4 + 2H_2S \rightarrow 2PbS + As_2O_5 + 3H_2O$$

As in the case of calcium arsenate, the arsenic acid formed by this reaction may cause serious plant injury. An excess of lime is frequently used with such combination sprays, and other correctives, such as proteinaceous materials, have been used with some success. Lead arsenate is used solely as a stomach poison, and has found its greatest use on fruit crops, particularly apples.

Basic lead arsenates are available commercially. They are of somewhat indefinite composition, but probably consist mainly of $Pb_4(PbOH)\cdot(AsO_4)_3\cdot H_2O$ and $Pb_5(PbOH)_2(AsO_4)_4$. These basic arsenates are less readily decomposed than the ordinary form of acid lead arsenate, and for this reason are used on certain plants, such as peaches, which are susceptible to arsenic injury.[42]

Paris Green. A complex of copper metarsenite and copper acetate with the formula $(CH_3COO)_2Cu\cdot 3Cu(AsO_2)_2$ is known as Paris green.[1] This compound was one of the first arsenicals to be used as an insecticide in commercial quantities. Paris green is a deep green color, and is rather readily broken down, even in the presence of water alone. The advent of newer, safer insecticides has largely displaced Paris green, and only small quantities of the compound are used at present.

Miscellaneous Arsenicals. Various arsenicals have been suggested as insecticides at one time or another.[9] Most of these are inferior to lead or calcium arsenate, and have never been widely used. Included in this group are aluminum arsenate; London Purple (a mixture of calcium arsenite and calcium arsenate); basic copper arsenate; copper arsenite, iron arsenates, and zinc arsenate. Magnesium arsenate is used in some areas for the control of the Mexican bean bettle. Its properties and reactions are similar to those of calcium arsenate.

Fluorine Compounds. *Fluorides.* Sodium fluoride, NaF, has been used for over half a century as an insecticide, mainly against cockroaches and other household insects. It is manufactured commercially from sodium carbonate and sodium silicofluoride

$$Na_2CO_3 + Na_2SiF_6 + H_2O \rightarrow 6NaF + H_2SiO_3 + 2CO_2$$

Other fluorides have been suggested as insecticides, but because they are soluble in water, they appear to be limited to special purposes, such as wood treatments, etc.[4]

Fluosilicates. Sodium fluosilicate, Na_2SiF_6, and potassium fluosilicate, K_2SiF_6, are highly toxic to certain species of insects,[20] but are not widely used on agricultural crops, because of their tendency to cause plant injury. The sodium salt finds considerable use as a mothproofing agent on fabrics, and a closely related compound, sodium aluminum fluosilicate, is also used for this purpose. Calcium, magnesium and barium fluosilicates have found considerable use as insecticides.[4] The latter salt in particular, $BaSiF_6$, is relatively insoluble in water, and has been used rather extensively against the Japanese bettle.

Fluoaluminates. Sodium fluoaluminate (sodium aluminum fluoride, cryolite, Na_3AlF_6) is a naturally occurring mineral which has long been used in the manufacture of aluminum. The compound may also be made synthetically from aluminum fluoride, ammonium fluoride and sodium chloride. Cryolite has been used successfully against a number of insects.[21] It is compatible with oils, soaps, sulfur, etc.; but not with alkaline materials such as Bordeaux mixture and lime sulfur.

Miscellaneous Inorganic Insecticides. A wide variety of inorganic compounds have been suggested as insecticides at various times. Of those which have attained some wide acceptance, mention should be made of tartar emetic (antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$), found effective against thrips on onions, gladioli, and citrus. Boric acid, H_3BO_3, and borax, $Na_2B_4O_7$, have been used in ant poisons and as fly preventatives in manure and refuse piles. Mercurous chloride (calomel, HgCl) and mercuric chloride ($HgCl_2$) are used to control cabbage maggot; and compounds of selenium and thallium have found some specialized uses in controlling insects, although they are not widely used.

ORGANIC INSECTICIDES

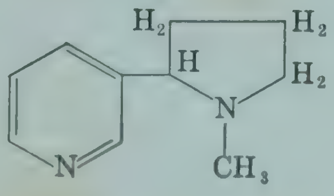
Plant Products

It is natural that attempts were made at an early date to find plants which were toxic or repellent to insects. Largely by trial and error three genera of plants were discovered to be potent insecticides—*Nicotiana, Chrysanthemum* (*Pyrethrum*) and *Derris.* Further, more careful scientific investigations have discovered other species possessing insecticidal properties, but these three species and a few closely related ones still furnish the bulk of our insecticides of plant origin. Several plants possess the desirable property of high toxicity to insects without being toxic to warm-blooded animals. For this reason they have been extremely popular as insecticides. Most plant insecticides act as contact poisons.

Nicotine. Tobacco powder and tobacco extracts were discovered to be toxic to certain insects over 250 years ago. The use of tobacco as an insecticide was therefore well established by the time of the discovery of nicotine as the active principle of tobacco in 1828. Nicotine has been isolated from a number of species, most of them belonging to the genus *Nicotiana.* Commercially, nicotine is produced from two species: the ordinary tobacco of commerce, *Nicotiana tabacum* Linn., and another, coarser, species, *Nicotiana rustica,* cultivated in certain parts of the world especially for the production of nicotine.[3, 24]

Chemistry of Nicotine and Related Compounds. The chemistry of nicotine and the other tobacco alkaloids has been given in detail by Busbey and McIndoo[3] and Jackson,[15] and will only be summarized here.

Nicotine, the predominant alkaloid of tobacco, has the formula



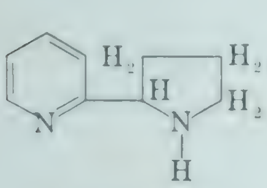
Nicotine (β-form)

The chemical designation for the compound is 3-(1-methyl-2-pyrrolidyl) pyridine. It was first isolated by Posselt and Reimann in 1828, and its structure determined in 1893. Pure nicotine is a water-white liquid having a sharp, burning taste, and is practically odorless. When exposed to air and light nicotine slowly darkens in color to a deep brown, and becomes more viscous at the same time. Pure nicotine boils at approximately 247° C. at atmospheric pressure, and has a density of 1.010 at 20° C.

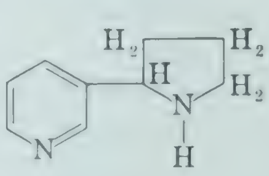
Naturally occurring nicotine is levorotatory, although its salts are dextrorotatory. It is miscible with alcohol and ether, and with water in all proportions below 60° C. and above 210° C. When mixed with water, hydrates are formed; these probably account for the miscibility. Several isomers of nicotine are possible.

Having two nitrogen atoms present in the heterocyclic structures, nicotine is basic in reaction, and readily forms salts with acids. Most of the nicotine sold in the United States is in the form of the sulfate. Salts of nicotine with various acids, as well as quaternary derivatives of nicotine, have been prepared and tested as insecticides. It may also be combined with bentonite, peat, and other materials to form complexes.[9] Some of these combinations have the virtue of prolonging the effective period of toxicity of nicotine insecticides.

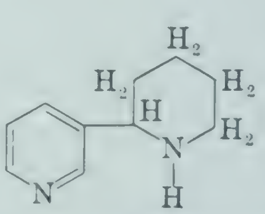
Nornicotine and Anabasine have been found in certain species of plants and have been tested as insecticides.[22, 36] They both resemble nicotine in chemical and physical properties, and are of the same order of toxicity to insects.



α-Nornicotine



β-Nornicotine



Anabasine (Neonicotine)

Preparation and Properties of Nicotine Insecticides. Nicotine is prepared commercially by treating the ground tobacco (usually tobacco waste is used) with alkali and distilling with steam. Tobacco dust, consisting of finely ground tobacco waste, is also used as an insecticide, as well as dusts containing nicotine absorbed on an inert carrier. However, most of the nicotine used for the control of insects is used as a spray.

Nicotine is one of the most poisonous alkaloids. It is absorbed readily through the skin and mucous membranes in mammals, and produces a paralysis of the nervous system. A similar action is observed in insects. It is most useful as a contact spray, and is commonly used against soft-bodied insects, particularly the aphids.

Pyrethrum. Although the date of the discovery of the insecticidal properties of pyrethrum is unknown, it is fairly clear that the dried flowers have been in use for well over a century. Only within the past twenty-five years, however, has the cultivation and application of pyrethrum reached extensive proportions.

The flower heads of several species of *Chrysanthemum* contain the active insecticidal principles. Dalmatia, Japan, and most recently Kenya have been extensive centers of production of these plants. Commercially, only one species, *Chrysanthemum cinerariaefolium*, is of importance. The flower heads are picked at the proper state of maturity, dried, and sold in compressed bales.

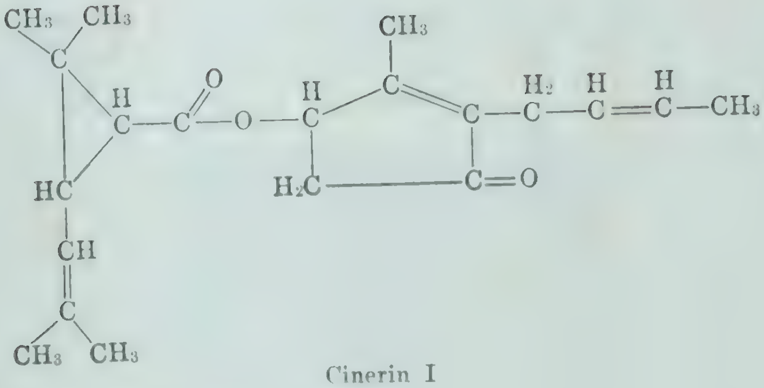
Flower head of pyrethrum, *Chrysanthemum cinerariaefolium*.

Chemistry of Pyrethrum. Staudinger and Ruzicka[40] first reported on the true chemical nature of the active principles of pyrethrum. These workers found two active compounds which they named pyrethrin I and pyrethrin II, respectively. These were esters of a keto-alcohol and two acids. Further work by LaForge[19] and associates has demonstrated the presence of two other esters, so that at present four compounds having insecticidal properties are known to exist in pyrethrum. (See next page).

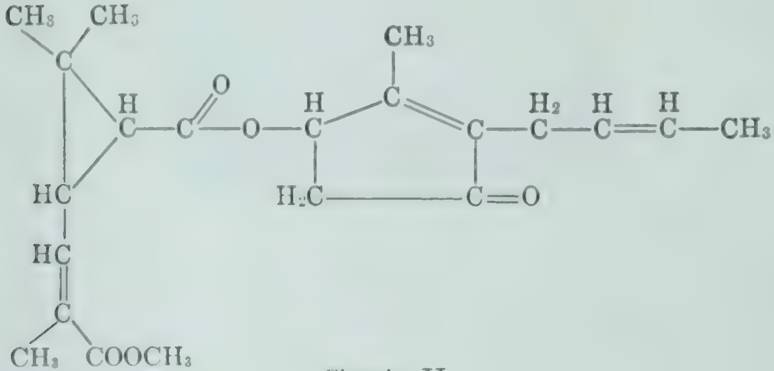
The pyrethrins and cinerins are all oily, viscous liquids, soluble in a variety of organic solvents, but not in water. They are decomposed rather readily, particularly in the presence of alkali, and for this reason pyrethrum preparations should never be compounded with soaps, lime, lime sulfur, and similar alkaline substances.[34] The pyrethrins and cinerins are decomposed during extended storage of the dried plant material, and flowers held for two years may lose as much as 40 per cent of their activity.[43]

A number of homologs of Cinerin I have been synthesized.[37a] One of these, the allyl homolog, has been prepared in commercial quantities and has been given the generic name of *allethrin*. Against certain insects allethrin is highly toxic, but against others the compound exhibits considerably less toxicity than the naturally occurring compound. It is probable that allethrin will find general use against household insects.

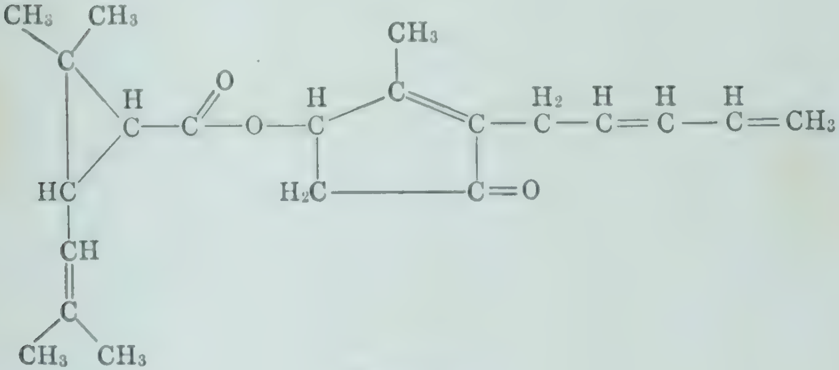
Preparation and Properties of Pyrethrum Insecticides. Most of the pyrethrum for insecticidal purposes goes into the production of household sprays. For this purpose the dried flower heads are extracted with a suitable solvent and the extract then diluted to the required concentra-



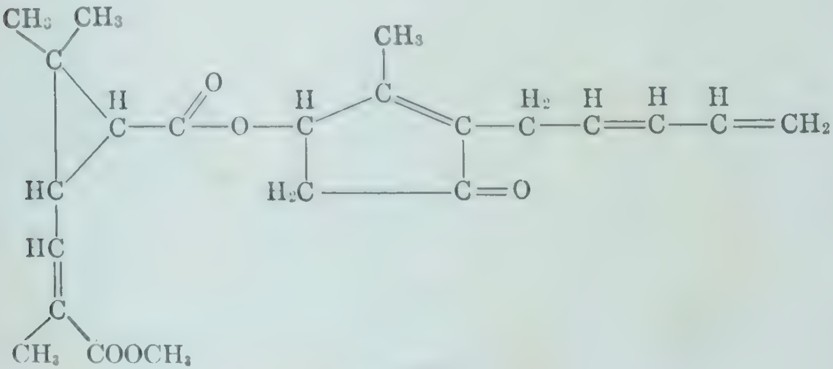
Cinerin I



Cinerin II



Pyrethrin I



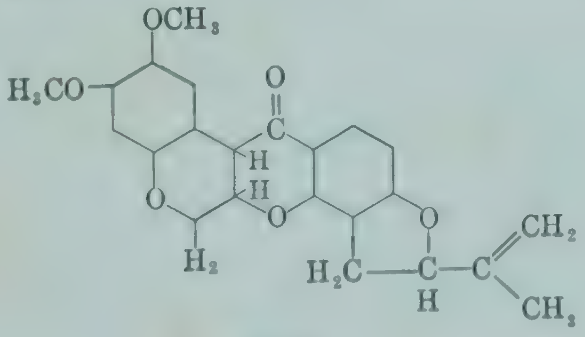
Pyrethrin II

tion with a light hydrocarbon oil. Such sprays are highly effective against flies, mosquitoes, and other insects commonly found in homes. They also find considerable use as livestock sprays. In compounding pyrethrum household sprays other materials are frequently added to enhance the insecticidal action of the pyrethrum. Rotenone is occasionally used for this purpose, and more recently DDT has been used. *Synergists,* such as sesamin, N-isobutyl hendecenamide, and certain piperonyl derivatives, are frequently added to increase the toxicity of the pyrethrum extract.[26]

Powdered pyrethrum, or dusts containing pyrethrum extracts absorbed on carriers are extensively used as household insecticides, and are finding an increasing use in the agricultural field. Pyrethrum extracts and concentrates are also a common component of aerosols intended for household use. Pyrethrum is practically nontoxic to warm-blooded animals, and for this reason is one of the most popular insecticides for use in homes, food processing plants, and on food crops. The subject of pyrethrum insecticides has been covered by Gnadinger[11] in a series of books.

Rotenone. Certain tropical and subtropical plant species have been used for many years as fish poisons, and to a limited extent as insecticides. About forty years ago the insecticidal properties of several of these species were investigated in more detail, and it was found that they possessed considerable value as pest control materials. The fish poison plants are all of the family Leguminosae, and comprise several different genera.[16] The most important of these are *Derris* and *Lonchocarpus,* but others possessing desirable qualities are *Tephrosia* (*Cracca*), *Mundulea,* and *Millettia.* Important species of *Derris* as sources of insecticides are *D. elliptica* and *D. malaccensis,* which are cultivated in British Malaya and the Netherlands East Indies. *Lonchocarpus nicou* and *L. utilis* are native of the Western hemisphere, and are commonly called *cube* (pronounced koobay'). Selection and breeding have raised the content of the active principle, rotenone, in several of the commercially developed species.

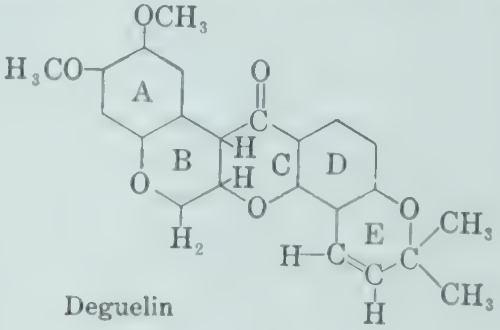
Chemistry of Rotenone. The main active principle of insecticidal value in the fish poison plants is rotenone,



Rotenone

Rotenone is a colorless compound, crystallizing in needles and hexagonal plates. It is dimorphic, the ordinary form melting at 163 to 164° C., the other at 181° C. It has the property of crystallizing from certain organic solvents with solvents of crystallization, similar to the water of crystallization in some inorganic compounds.[18] When exposed to light and air, rotenone undergoes decomposition, with a corresponding loss of toxicity to insects.

For some time is was considered that rotenone was the sole active constituent of this group of insecticidal plants. Extended studies on the chemistry of the plants have revealed the presence of several others: these are generally grouped together under the name *rotenoids*. These exhibit different degrees of toxicity toward insects, but as a whole they contribute materially toward the insecticidal value of the plants. Mention should be made of deguelin, sumatrol, toxicarol, and malaccol in this connection.[19]


OCH3
H3CO
A
B
C
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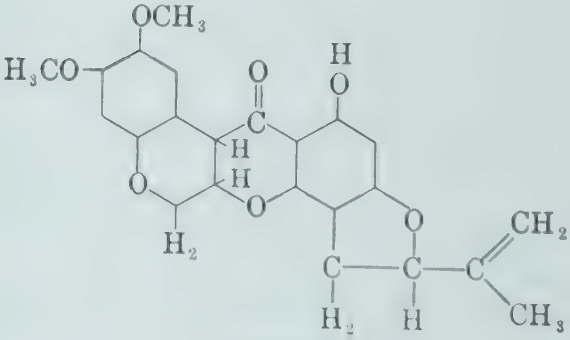
CH3

Deguelin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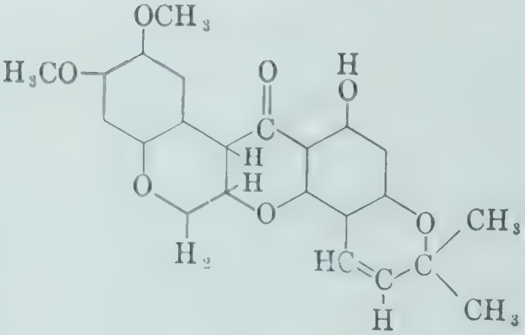
Sumatrol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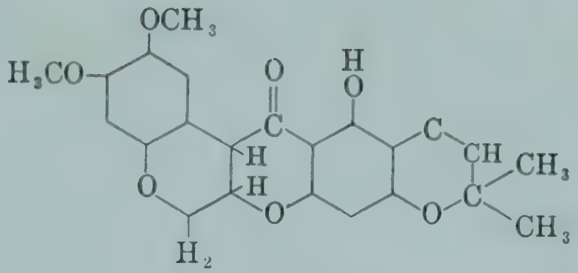
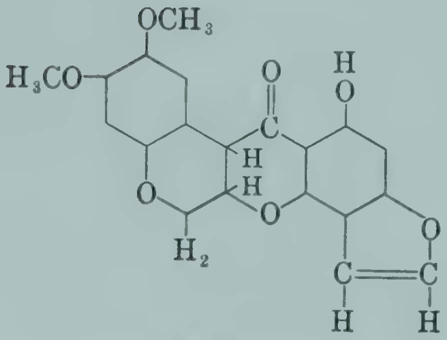
α-Toxicarol



β-Toxicarol



Malaccol

Of these, apparently deguelin is most toxic to insects, although considerably inferior to rotenone in this respect. None of these compounds is highly toxic to higher animals, a fact which makes rotenone, like pyrethrum, a particularly desirable insecticide for general use.

Preparation and Properties of Rotenone Insecticides. For use as dusts, the most commonly used form of rotenone is the ground roots of the fish poison plants, diluted to a suitable concentration with an inert carrier, such as bentonite or talc. Impregnated dusts are also available, made from concentrated extracts of the roots in organic solvents. Similar extracts are commonly used to prepare emulsions. Rotenone finds its principal use as an insecticide on agricultural crops, particularly those intended for food use. The Mexican bean bettle, cabbage worms, pea aphids, and other insects attacking vegetables are readily controlled by rotenone sprays and dusts.

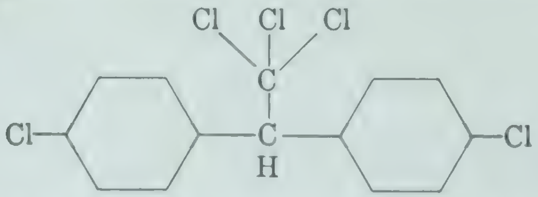
Other Plant Insecticides. Although thousands of plant species have been tested for insecticidal properties, only a few have been sufficiently effective to warrant their commercial exploitation. Hellebore (*Veratrum album* or *V. viride*) and Sabadilla (*Schoenocaulon officinale*) have been found to be toxic to certain species of insects. The active principles in these plants appear to be similar, and to be alkaloidal in nature. *Ryania speciosa*, a tropical American plant, has recently been suggested as an insecticide for the control of the corn borer. *Quassia* species, *Pachyrrhizus erosus*, and a number of other plants have been suggested as promising insecticides at one time or another, but have never been extensively tested. The reader is referred to the compilations of McIndoo [25] and Frear [8, 38] for a more complete listing of insecticidal plants.

Synthetic Organic Insecticides

In contrast to the inorganic and plant insecticides, the synthetic organic group of insecticides is of very recent origin. Many of the synthetic organic compounds used for pest control are so new that their properties have not been fully explored: further research and practical experience will permit more definite statements on their particular areas of usefulness and their limitations.

DDT [2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane]. This compound, one of the first synthetic organic compounds to receive wide acceptance as an insecticide, was first synthesized by Zeidler in 1874. Research studies carried out in Switzerland just prior to World War II indicated the great potential value of the compound as an insecticide. Stimulated by the wartime needs, a tremendous amount of research was conducted on DDT in a relatively short period of time: as a result our knowledge of the chemical and biological properties of this subseance is more nearly complete than in the case of any other synthetic organic insecticide.[10]

Pure 2,2-bis(*p*-chlorophenyl)-1,1,1,-trichloroethane is a white crystalline compound occurring in long tabular needles. It has a melting point of 108.5–109.0° C., and a density of 1.556. It is soluble in a nunber of organic solvents, but is insoluble in water. The structural formula is



Commercially, DDT is made by reacting chloral and chlorobenzene in the presence of sulfuric acid.[27]

$$Cl_3CCHO + 2C_6H_5Cl \rightarrow Cl_3CCH(C_6H_5Cl)_2 + H_2O$$

The commercial product (Technical DDT) contains upward of 70 per cent of 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane, which is frequently designated as *p,p'*-DDT for convenience, together with a number of related products. The chief one of these is *o,p'*-DDT (2-*o*-chlorophenyl-2-*p*-chlorophenyl-1,1,1-trichloroethane), which has practically no insecticidal value.[14] Other, more highly refined grades of DDT are commercially available for special uses, but the majority of insecticidal products containing DDT are made from the technical grade.

Chemically, DDT is quite stable, except in the presence of alkalies and certain metallic salts. With alkaline materials, DDT is dehydrochlorinated, the product being 2,-2-bis(*p*-chlorophenyl)-1,1-dichloroethylene, which had inferior insecticidal properties. Salts of iron, chromium, aluminum and other metals catalyze the dehydrochlorination of DDT, and result in the formation of the same product. For these reasons DDT should never be compounded or mixed with alkaline materials, such as lime, nor should it be stored in steel containers. Certain types of diluents used for making insecticide dust formulations are alkaline enough to cause some decomposition of DDT.[7]

Preparation and Properties of DDT Formulations.[45] DDT acts as an insecticide in a somewhat different manner than the materials discussed up to this point. The solid material is highly toxic to insects which come in contact with it, and advantage is taken of this property in the formulation of residual sprays and dusts. By the proper choice of diluent, it is possible to deposit DDT on surfaces where insects congregate: the deposits so prepared are toxic for relatively long periods of time. The commonly used insecticide formulations of DDT are:

1. Solutions in organic solvents to be used directly.
2. Concentrated solutions in organic solvents, containing emulsifying agents, to be mixed with water, and applied as dilute emulsions.
3. Mixtures with dry powders, with added wetting agents, to be applied as water suspensions.
4. Mixtures with dry powders, to be applied as dusts.
5. Mixtures (or solutions) with propellant gases under pressure, to be applied as aerosols.
6. Mixtures (or solutions) in paints, polishes, etc.
7. Mixtures (or solutions) used for impregnating fabrics, paper, etc.

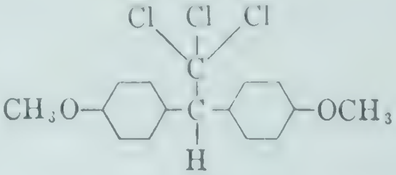
Of these, the first four are the most commonly used. For household use, 5 per cent solutions of DDT in a highly refined petroleum oil are commonly used. Some sprays of this type contain other toxicants, such as pyrethrum extract, organic thiocyanates, etc., for immediate knockdown of insects. Concentrated emulsions and wettable powders are employed where a visible residue is not objectionable, as in barns or on plants. Dusts are used to control animal parasites and on agricultural crops. In this connection, it has been found that DDT, when applied on or fed to dairy cattle, is secreted in the milk produced.[46] Since the continued ingestion of DDT may cause toxic manifestations in animals or humans, the use of DDT formulations on lactating dairy animals, or on forage crops fed to them, is not permitted in order to protect the public health.

Aerosols containing DDT are used frequently for the control of insects in homes, factories, and similar enclosed areas. These applications serve only as "space treatments" and do not leave enough residual deposits to be effective for any length of time. Some paints have been formulated with DDT, and have proved effective; this application, along with the treatment of fabrics, paper, etc., to prevent insect damage, has been tried only in a rather limited way. They offer considerable promise for the future, however.

Like many other insecticides, DDT is toxic to higher animals as well as insects.[28] It may be absorbed through the skin from solutions (but apparently not appreciably when applied as a dry solid). The order of acute toxicity to higher animals appears to be relatively low; one dose of several hundred grams having been fed to large domestic animals without fatal effects. Continuing doses of much smaller magnitude may cause chronic toxicity, however, and care should be taken that forage crops, fruits, vegetables, and milk should not be contaminated with any considerable amounts of DDT. It has been suggested that 7 p.p.m. of DDT on articles of food eaten irregularly or 1 p.p.m. on foods eaten as a regular part of the daily diet may be safe limits.

Compounds Related to DDT. The discovery of the remarkable insecticidal properties of DDT naturally has stimulated a great deal of research on related compounds. Of the many which have been synthesized and tested, several show promise as commercial insecticides.

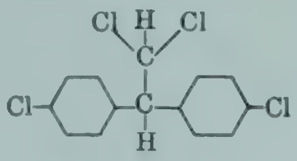
Methoxychlor (2,2-di-*p*-anisyl-1,1,1-trichloroethane). This compound having the formula



is closely related to DDT, having the two chlorine atoms attached to the phenyl groups replaced by methoxy ($-OCH_3$) groups. In general, it has similar insecticidal properties to DDT, but is considerably less toxic to higher animals.[33] It probably will find considerable use on situations where it is desirable to avoid highly toxic residues.

Methoxychlor has chemical and physical properties similar to those of DDT.

TDE [DDD;-1,1-bis(*p*-chlorophenyl)-2,2-dichloroethane] having the formula

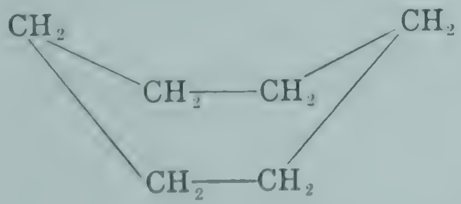


has been found to be toxic to a number of insects. It has similar properties to DDT, and appears to be highly toxic to certain species of insects.

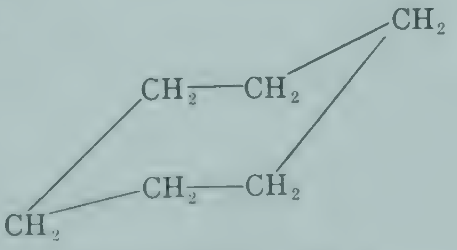
Of the many other relatives of DDT which have been prepared and tested as insecticides, none has been produced in commercial quantities in this country. The fluorine analog was used to some extent in Germany during the war. This compound was an effective insecticide, but was relatively expensive to manufacture.

Hexachlorocyclohexane (Benzene hexachloride; BHC). Like DDT, this compound was known to the chemists long before its insecticidal properties were discovered. Research work in England and France in 1942 indicated that of the isomeric forms of benzene hexachloride, one (designated as gamma) possessed excellent insecticidal properties.[39] This material is now commercially available and is widely used.

When benzene is chlorinated in the presence of light it accepts six atoms of chlorine, forming an addition compound having the formula $C_6H_6Cl_6$. The main product of the reaction is 1,2,3,4,5,6-hexachlorocyclohexane. In this compound one hydrogen atom and one chlorine atom are attached to each carbon in the ring. This molecule may exist in sixteen possible stereoisomeric forms. In order to understand the structural configuration of the isomers of 1,2,3,4,5,6-hexachlorocyclohexane, it is necessary to consider the molceules as three dimensional bodies. Cyclohexane may exist in two forms, since it is not possible for the six carbon atoms in the ring to lie on one plane:

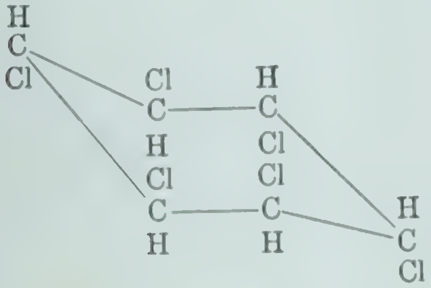


Cis ("boat") form of cyclohexane

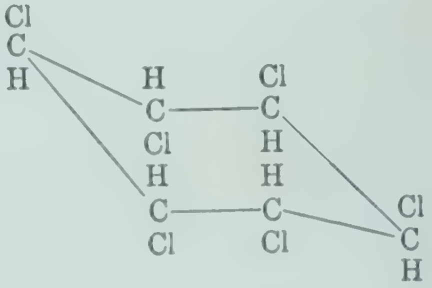


Trans ("chair") form of cyclohexane

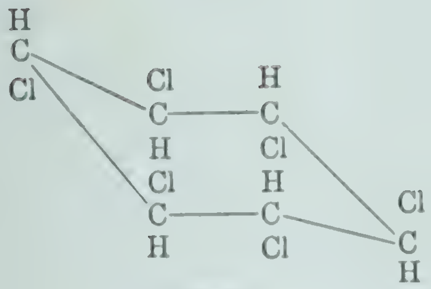
When chlorine and hydrogen atoms are attached to each carbon, it may be seen that it is possible to have a structure in which all of the hydrogen atoms lie *above* the carbon atoms, while all of the chlorine atoms will lie *below* them. The different combinations, each having a different arrangement of attached atoms, account for the possible isomers. Actually, five isomeric forms of 1,2,3,4,5,6-hexachlorocyclohexane have been isolated: the postulated structures for the four present in largest amounts are as follows:



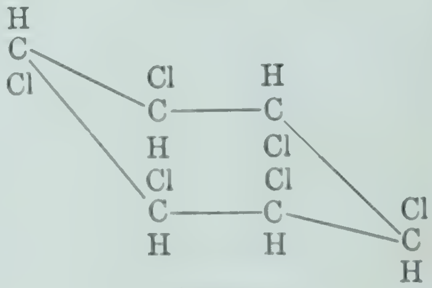
Alpha I



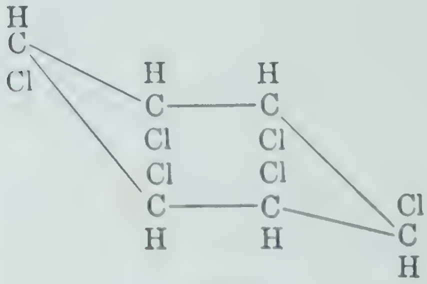
Alpha II



Beta



Gamma



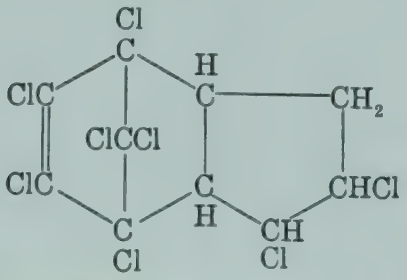
Delta

The gamma isomer has been found to be the only one possessing appreciable toxicity to insects. This occurs to the extent of 10–12 per cent in the crude product resulting from the chlorination of benzene. The mixture of isomers has a very persistent, musty odor, which makes it undesirable for use on food crops or in dwellings.

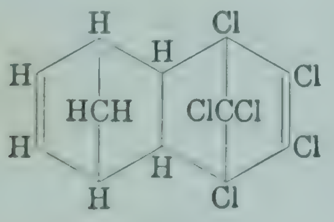
Recently it has been found possible to separate the gamma isomer in substantially pure form. A product containing 99 + % of the gamma isomer has been designated as *Lindane.* This material has no appreciable odor and is now being used extensively for the control of houseflies and many other insects.

The pure gamma isomer is a white, crystalline solid, with a melting point of 112.5° C. It is insoluble in water, but soluble in organic solvents. It may be formulated as solutions, dusts, emulsion concentrates and wettable powders. Like DDT, benzene hexachloride is dehydrochlorinated in the presence of alkalies, and for this reason it should not be formulated with substances having a basic reaction.

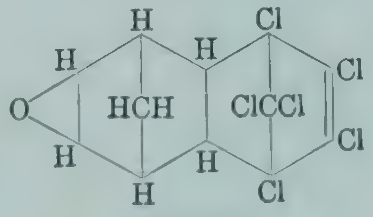
Chlordane (1,2,4,5,6,7,8,8-octachloro-4,7-methano-3a,4,7,7a-tetrahydroindane). This compound having the formula



is a viscous liquid. The commercial product is a mixture of the indane derivative and several related compounds. Apparently all of these compounds possess insecticidal properties. It may be formulated in the same was as DDT and benzene hexachloride, and, like these compounds, is decomposed by alkali. It is highly toxic to insects.[17] Two other related compounds, *aldrin* and *dieldrin,* chemically 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene and 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene, respectively, have shown high toxicity to insects.



Aldrin



Dieldrin

Aldrin is a white crystalline solid, m.p. 104–104.5° C., freely soluble in benzene, acetone, petroleum base oils, and hexane, but less soluble in methanol and insoluble in water. It is not affected by the concentrations of alkalies or acids encountered in practical use. The toxicity to insects is very high, and it is toxic to higher animals: from solutions it may be absorbed through the skin. Upon exposure to the air on plant surfaces, however, aldrin disappears in 3 weeks or less, so that there is not great danger of residue hazards if sufficient time elapses between the last application and harvest.

Dieldrin is also a white crystalline solid, m.p. 175–176° C., freely soluble in acetone and benzene, less soluble in other organic solvents, including base oil, and insoluble in water. Like aldrin, dieldrin is highly toxic to both insects and higher animals. It possesses a long period of residual activity, however, and apparently persists for a considerable period after application. Dieldrin is not affected by the concentrations of acids or alkalies normally encountered. Both aldrin and dieldrin are formulated in the same way as DDT.

Toxaphene (chlorinated camphene). This material, having an approximate empirical formula of $C_{10}H_{10}Cl_8$, is apparently produced by chlorinating terpenes. The commercial material is a waxy solid, soluble in organic solvents. Toxaphene is an efficient insecticide against certain agricultural pests.[41]

Organic Phosphorus Compounds. *Tetraethyl Pyrophosphate* (TEPP). This compound, thought to have the structure

$$(C_2H_5O)_2PO{-}O{-}OP(OC_2H_5)_2,$$

can be prepared by reacting phosphorus oxychloride and triethyl phosphate.

$$5(C_2H_5)_3PO_4 + POCl_3 \rightarrow 3C_2H_5Cl + 3(C_2H_5)_4P_2O_7$$

It may also be made from phosphorus oxychloride and ethyl alcohol.

This material is apparently the principal active insecticidal component in a mixture formerly designated as "hexaethyl tetraphosphate."[37]

Tetraethyl pyrophosphate as commercially produced is a liquid. It is usually employed as a contact insecticide, and is mixed with water as a spray. When mixed with water, it hydrolyzes rapidly and loses its toxicity. Although the material is also highly toxic to higher animals, this property of hydrolysis to relatively harmless decomposition products makes it unlikely that spray residues from this compound will present a public health problem. In concentrated form, however, it is readily absorbed, through the skin, and it should be handled with great care.

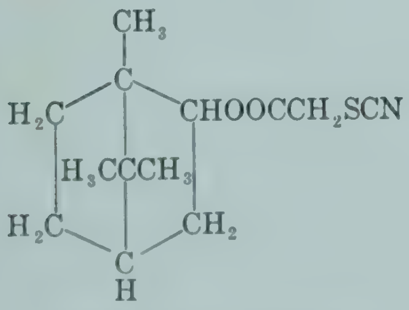
Parathion. This compound, O,O-diethyl-O-*p*-nitrophenyl thiophosphate, may be made by reacting thiophosphoryl monochloride and treating the resulting product with a chlorobenzene solution of sodium *p*-nitrophenate.

$$2C_2H_5ONa + PSCl_3 \rightarrow (C_2H_5O)_2PSCl$$
$$(C_2H_5O)_2PSCl + NaOC_6H_4NO_2 \rightarrow (C_2H_5O)_2PS{-}O{-}C_6H_4NO_2$$

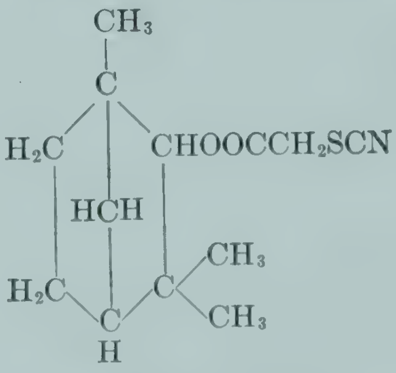
Parathion is a yellow liquid with an estimated boiling point of 375° C. at 760 mm. It is very slightly soluble in water, but freely miscible with a number of esters, ethers, and alcohols. It is relatively insoluble in petroleum fractions.

This material is highly toxic as a contact insecticide to many species. It is also extremely toxic to higher animals, and should be treated with great caution when in concentrated form. It is formulated as wettable powders and dusts, and quite rapidly loses its toxicity on exposure to air. Applications to most crops made one month or more before harvest usually result in negligible residues.

Nitrogen Compounds. *Organic Thiocyanates.* Several organic thiocyanates have attained wide use as contact insecticides, particularly in household sprays. For this purpose they are usually dissolved in a highly refined petroleum oil, and are used as substitutes or extenders for pyrethrum (see later section). Brief mention should be made of lauryl thiocyanate, $CH_3(CH_2)_{10}CH_2SCN$, 2-[2-(butoxy)ethoxy] ethyl ester of thiocyanic acid, $C_4H_9OCH_2CH_2OCH_2CH_2SCN$, and 2,2′-dithiocyano diethyl ether, $NCSCH_2CH_2OCH_2CH_2SCN$. The latter compound has had considerable use on agricultural crops. Isobornyl thiocyanoacetate and fenchyl thiocyanoacetate have also been used against household and livestock pests.



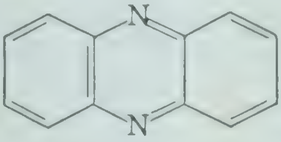
Isobornyl thiocyanoacetate



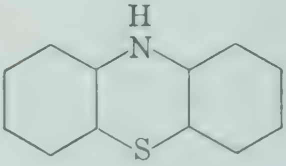
Fenchyl thiocyanoacetate

Nitro Compounds. Organic nitro compounds have found considerable use as ineseticides, as well as fungicides and herbicides. (See Chapters XXI and XXII.) Dinitro-*o*-cresol (4,6-dinitro-*o*-cresol; DN or DNOC) has been used as a dormant spray ingredient, but its high phytotoxicity prevents its use on growing plants. 2,4-Dinitro-6-cyclohexylphenol (DNOCHP), which possesses greater toxicity to certain insects, has superseded the older material to a large extent. The cyclohexyl derivative is also available as the dicyclohexylamine and triethanolamine salts. Certain related compounds have recently appeared on the market, and it is claimed that these are less phytotoxic than the materials available earlier.

Heterocyclic Compounds. A number of compounds having heterocyclic nitrogen-containing structures have been found to be toxic to insects. Phenazine and phenothiazine

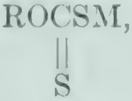


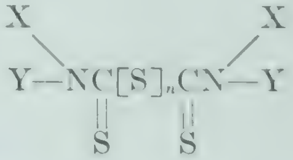
Phenazine



Phenothiazine

are examples of this class of compounds. The latter material appears to be toxic to certain fruit insects, and was used commercially before the discovery of the insecticidal properties of DDT.

Miscellaneous Synthetic Organic Compounds. Space permits only brief mention of a few of the many synthetic organic compounds which have been used as insecticides. The alkali metal xanthates, having the general formula  $\mathrm{RO}\underset{\underset{\displaystyle \mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SM}$, the thiuram sulfides,



have both been sold as commercial insecticides. Amines, azo compounds, xanthone, and phenoxathiin appear to be relatively toxic to certain insect species, and considerable research has been reported on them. A number of compounds have been found to act as synergists for pyrethrum extract and are now commonly used for this purpose (see p. 505).

Many synthetic organic compounds which may be potential insecticides have not been mentioned. For a fuller discussion of this subject, the reader is referred to the compilations and books on the subject.[8, 9]

THE OILS

Oils of plant and animal origin, as well as petroleum oils, have been used as insecticides. Chemically, of course, the plant and animal oils are glyceride esters of fatty acids, and differ greatly from the petroleum fractions, which consist mainly of hydrocarbons. For a number of reasons, not the least of which is cost, the plant and animal oils and their component fatty acids have not been used extensively as insecticides. In this chapter the discussion will be limited largely to the various petroleum oils used for insecticidal purposes.

Kerosene-type Oils. The kerosene fractions are made by distillation from the crude oil, and consist mainly of hydrocarbons having from 10 to 16 carbon atoms per molecule. The viscosity is low, and they usually have a flash point of at least 150° F.

The greatest use for kerosenes today is in the preparation of household and livestock sprays. For this purpose the oil must be subjected to a rather drastic refining process to remove foreign colors and odors. This is usually done by treating the oil with concentrated sulfuric acid, followed by the removal of the water-soluble reaction products. Kerosenes refined in this way are bland, colorless, and odorless. They are used as solvents for pyrethrum extracts, the organic thiocyanates, DDT, and many other toxicants. The kerosene itself is a contact insecticide, and, in addition, furnishes a convenient carrier for dispersing the more active ingredients.

"Light and Medium" Oils. These oils are intermediate fractions derived from the distillation of the stock and have a viscosity range from 40 to 85 seconds Saybolt. These oils are used mainly as "summer" sprays on fruit trees and are sold as concentrated emulsions or as mixtures with emulsifiers ("ready mix") which may be diluted with water for application. Certain types of foliage are susceptible to injury from oil sprays and this tendency has been related to the amount of unsaturated compounds occurring in the oil. A good measure of these is the *unsulfonatable residue,* which, if large, indicates a high percentage of saturated hydrocarbons, and hence an oil which is relatively safe to use. It has recently been found that oils containing a high percentage of paraffinic hydrocarbons are more efficient insecticides than those containing aromatic or naphthenic compounds.[31] This is of considerable practical importance.

"Heavy" Oils. This classification usually includes those fractions having a viscosity greater than 85 seconds Saybolt. They are mainly used for application to dormant vegetation, and hence do not need to be as highly refined as the types mentioned previously. They are used to destroy insect eggs which overwinter on the bark and twigs of trees and shrubs, and frequently are used in combination with other materials, such as the dinitro compounds.

Coal Tar Oils. These materials, derived from the destructive distillation of coal, contain a number of organic compounds, including substances having acidic and basic properties.[44] In the past, coal tar distillates have been used as dormant sprays in much the same way as the heavy petroleum oils. At present, however, very little of this material is used for this purpose. Certain of the creosote fractions of coal tar find considerable use for treating timbers to prevent insect and fungus damage.

Fatty Acids and Soaps. As mentioned earlier, these materials are fairly efficient contact insecticides, but their use has been discouraged by their relatively high price, and because newer, more efficient materials are available. The soaps are still used as wetting agents to provide better coverage for aqueous solutions and suspensions of other insecticides, and are useful for this purpose.

FUMIGANTS

Fumigants are defined as those materials which exert their toxic action in the vapor state. They may be applied as solids, liquids, or gases, but must volatilize and diffuse readily if they are to be efficient insecticides.

Hydrocyanic Acid (hydrogen cyanide, prussic acid).[6] This compound, HCN, is a colorless gas at temperatures above 26° C. As a fumigant it may be applied directly as a liquid or gas. The gas may be generated by the chemical reaction of an acid on one of the alkali metal cyanides, for example, sodium cyanide, according to the reaction

$$NaCN + H_2SO_4 \rightarrow NaHSO_4 + HCN$$

Calcium cyanide reacts with moisture of the air to release hydrocyanic acid gas, and this method is frequently used because of its simplicity.

Hydrocyanic acid is an efficient insecticide, but is highly toxic to all forms of life as well. It should never be used by inexperienced persons, and wherever it is employed, all possible safety precautions should be observed.

Chloropicrin. Having a formula of CCl_3NO_2, this compound is a liquid at ordinary temperatures, but readily volatilizes to form a gas with good insecticidal properties.[35] In recent years, this material has been widely used as a soil fumigant. It has the advantage over certain other toxic gases, in that it causes nausea in relatively low concentrations, so that its presence may be noted quickly and unmistakably.

Carbon Disulfide and Carbon Tetrachloride. These materials are both volatile liquids, and have been used for small-scale fumigations for many years. Carbon disulfide is not only highly toxic to insects, but it is highly inflammable, and must be used with extreme caution. Carbon tetrachloride is not inflammable, but is less effective as an insecticide.

Methyl Bromide (CH_3Br). Although this compound has a boiling point of 3.5° C., it is easily handled as a liquid in cylinders under low pressure, and is thus convenient to apply. It is relatively toxic to all animals, and should be used with caution. The principal uses are for mill and industrial fumigation, but it has been used on nursery stock and other agricultural applications.[2]

Chlorinated Fumigants. A number of chlorinated compounds have been used as fumigants. Some of the more important of these are dichloropropane-dichloropropene (D–D) mixture; dichloroethyl ether, $ClCH_2$-

$CH_2OCH_2CH_2Cl$; propylene dichloride, $CH_2ClCHClCH_3$; 1,1-dichloro-1-nitroethane, $H_3CC(Cl)_2NO_2$; ethylene dichloride, $C_2H_4Cl_2$; and hexachloroethane, C_2Cl_6. These have special applications, and are useful fumigants. *D–D mixture* is largely used as a soil fumigant.[5]

Ortho- and Paradichlorobenzenes. These two compounds, made by chlorinating benzene, are widely used fumigants. Orthodichlorobenzene is a liquid at ordinary temperatures, and has a density of 1.3048. It is used mainly for termite control, being applied to timbers and foundations of buildings where these insects are prevalent. Paradichlorobenzene is a solid, m.p. 56° C., and is used in large quantities as a means of controlling the clothes moth. The crystals are scattered freely in closets, trunks, and other storage areas, where they slowly volatilize.

Naphthalene. This compound is a by-product of the coal tar industry, and is familiar to most householders as "moth balls" or "moth flakes." Naphthalene is a solid, m.p. 80° C., and is applied in the same way as paradichlorobenzene. Some 15,000,000 pounds of naphthalene are used annually in the United States against the clothes moth.

BIBLIOGRAPHY

1. Avery, S., *J. Am. Chem. Soc.* **28**: 1155 (1906).
2. Busbey, R. L., *U. S. Dept. Agr., Bur. Entomol. Plant Quarantine* **E–618** (1944).
3. Busbey, R. L., and McIndoo, N. E., *U. S. Dept. Agr., Bur. Entomol. Plant Quarantine* **E–384** (1936).
4. Carter, R. H., and Busbey, R. L., *U. S. Dept. Agr., Bur. Entomol. Plant Quarantine* **E–466** (1939).
5. Carter, W., *J. Econ. Entomol.* **38**: 35 (1945).
6. Cupples, H. L., Young, H. D., and Busbey R. L., *U. S. Dept. Agr., Bur. Entomol. Plant Quarantine* **E–354**, **E–368**, **E–381**, **E–493**, and **E–494** (1930–39).
7. Fleck, E. E., and Haller, H. L., *Ind. Eng. Chem.* **37**: 403 (1945).
8. Frear, D. E. H., "A Catalogue of Insecticides and Fungicides." Vol. I. Chemical Insecticides. Vol. II. Chemical Fungicides and Plant Insecticides. Waltham, Mass., Chronica Botanica Co. (1948).
9. Frear, D. E. H., "Chemistry of Insecticides, Fungicides and Herbicides." New York, D. Van Nostrand Co., Inc. (1948).
10. Froelicher, V., *Soap* **20**(7): 115 (1944).
11. Gnadinger, C. B., "Pyrethrum Flowers," 2nd ed. and Suppl. Minneapolis, McLaughlin Gormley King Co. (1936 and 1945).
12. Goodwin, W., and Martin, H., *J. Agr. Sci.* **16**: 596 (1926).
13. Haller, H. L., Goodhue, L. D., and Jones, H. A., *Chem Reviews* **30**: 33 (1942).
14. Haller, H. L., et al., *J. Am. Chem. Soc.* **67**: 1591 (1945).
15. Jackson, K. E., *Chem. Reviews* **29**: 123 (1941).
16. Jones, H. A., *U. S. Dept. Agr., Bur. Entomol. Plant Quarantine* **E–571** (1942).
17. Kearns, C. W., Ingle, L., and Metcalf, R. L., *J. Econ. Entomol.* **38**: 661 (1945).
18. LaForge, F. B., Haller, H. L., and Smith, L. E., *Chem. Reviews* **12**: 181 (1933).
19. LaForge, F. B., et al., *J. Org. Chem.* **12**: 199 (1947); *J. Am. Chem. Soc.* **70**: 3707 (1948).

20. Marcovitch, S., *Ind. Eng. Chem.* **18**: 572 (1926).
21. Marcovitch, S., and Stanley, W. W., *Tenn. Agr. Expt. Sta. Bull.* **140** (1929).
22. Markwood, L. N., *U. S. Dept. Agr., Bur. Entomol. Plant Quarantine* **E–561** (1942).
23. McDonnell, C. C., and Smith, C. M., *J. Am. Chem. Soc.* **38**: 2027 (1916).
24. McIndoo, N. E., Roark, R. C., and Busbey, R. L., *U. S. Dept. Agr., Bur. Entomol. Plant Quarantine* **E–392** (1936).
25. McIndoo, N. E., and Sievers, A. F., *U. S. Dept. Agr. Dept. Bull.* **1201** (1924).
26. Mentzer, R. L., Daigh, F. C., and Connell, W. A., *J. Econ. Entomol.* **34**: 182 (1941).
27. Mosher, H. S., Cannon, M. R., Conroy, E. A., Van Strien, R. E., and Spalding, D. P., *Ind. Eng. Chem.* **38**: 916 (1946).
28. Neal, P. A., et al., *Supplement No.* **177** to *U. S. Public Health Repts.* (1944).
29. Patten, A. J., and O'Meara, P., *Mich. Quart. Bull.* **2**: 83 (1919).
30. Pearce, G. W., and Avens, A. W., *J. Am. Chem. Soc.* **59**: 1258 (1937).
31. Pearce, G. W., Chapman, P. J., and Frear, D. E. H., *Ind. Eng. Chem.* **40**: 284 (1948).
32. Pearce, G. W., and Norton, L. B., *J. Am. Chem. Soc.* **58**: 1104 (1936).
33. Prill, E. A., Hartzell, A., and Arthur, J. M., *Science* **101**: 464 (1945).
34. Roark, R. C., *J. Econ. Entomol.* **23**: 460 (1930).
35. Roark, R. C., *U. S. Dept. Agr., Misc. Pub.* **176** (1934).
36. Roark, R. C., *U. S. Dept. Agr., Bur. Entomol. Plant Quarantine* **E–537** (1941).
37. Rohwer, S. A., and Haller, H. L., *Pests* **16**: No. 8, 12 (1948).
37a. Schechter, M. S., Green, N., and LaForge, F. B., *J. Am. Chem. Soc.* **71**: 1517 (1949).
38. Seiferle, E. J., and Frear, D. E. H., *Ind. Eng. Chem.* **40**: 683 (1948).
39. Slade, R. E., *Chem. Ind. No.* **40**: 314 (1945).
40. Staudinger, H., and Ruzicka, L., *Helv. Chim. Acta* **7**: 177, 201, 212, 236, 245, 377, 390, 406, 442, 448 (1924).
41. Stearns, L. A., Parker, W. L., MacCreary, D., and Connell, W. A., *J. Econ. Entomol.* **40**: 79 (1947).
42. Streeter, L. R., and Thatcher, R. W., *Ind. Eng. Chem.* **16**: 941 (1924).
43. Weed, A., *Soap* **16**(7): 101 (1940).
44. Weiss, J. M., and Downs, C. R., *Ind. Eng. Chem.* **15**: 1022 (1923).
45. West, T. F., and Campbell, G. A., "DDT, the Synthetic Insecticide." London, Chapman and Hall Ltd. (1946).
46. Wilson, H. F., Allen, N. N., Bohstedt, G., Bethail, J., and Lardy, H. A., *J. Econ. Entomol.* **39**: 801 (1946).

Chapter XXI

FUNGICIDES

Donald E. H. Frear

The Pennsylvania State College, State College, Pa.

Second only to insects, plant diseases cause the greatest economic losses on agricultural crops. These diseases are caused by a number of organisms, chief of which are the bacteria, viruses and fungi. Bacterial and virus infections, since they are usually within the plant itself, are difficult to control. Fungi, on the other hand, most frequently have one or more stages of their life cycle on the exterior of the plant, and may thus be controlled by chemical means. The chemicals used for this purpose are designated as fungicides.

Various classifications for fungicides have been proposed. One of the most useful classifications is similar to that used for insecticides. *Protective fungicides* can be defined as those materials which are applied prior to fungus infection, and serve to protect the plant from such an infection. *Eradicant fungicides,* by contrast, are applied after the plant has been infected by fungi, and, as the name implies, serve to eradicate the disease. A distinction is frequently made between *fungicides* and *fungistats,* the latter being those materials which prevent the growth of fungi without actually destroying the organism.

Most plant disease fungi are disseminated as spores, carried by the wind, water, or other mechanical means. In this respect they present a different problem from insects, which are usually capable of moving from one place to another under their own power. This does not mean that fungi are more easily controlled than insects, but the fact is mentioned to indicate that it is frequently possible to adapt the method of control to fit the conditions and the peculiarities of the pest to be controlled.

In the discussion of insecticides (Chapter XX) it was pointed out that the choice of toxicant for a particular insect depended upon a number of factors. The same is true for the fungicides. Since fungi are themselves plants, in most cases it is necessary to find a chemical which will selectively destroy the parasite without injury to the host. The problem of destroying one plant without injury to another with which it is in intimate contact is often difficult in the extreme, and such factors as state of growth of each plant variety, temperature, humidity, and many others must be considered carefully before the final decision on application materials and procedure can be made.

As stated in the previous chapter, the present discussion will not include recommendations for the control of specific pests. The chemical, physical and general biological properties of the commonly used fungicides will be considered in the pages to follow.

INORGANIC FUNGICIDES

Sulfur and Its Compounds. Sulfur and several of its inorganic compounds are among the most widely used fungicides. It should be noted that in many cases these same compounds also act as insecticides and acaricides. Rather than repeat the discussion of these same materials, they will be considered in this chapter, since at present they are more commonly used to destroy fungi than insects.

World consumption of sulfur for pest control purposes is approximately one-half billion pounds annually. The greater portion of this is used in the fruit-growing countries.

Elemental Sulfur. Free sulfur occurs in deposits in many parts of the world. The element may exist in several crystalline varieties, and two allotropic forms—monoclinic and rhombic—the latter being the stable form. The specific gravtiy of the rhombic form is 2.07 and the melting point 112.8° C. It is practically insoluble in water, slightly soluble in alcohol and ether, and freely soluble in carbon disulfide and sulfur chloride.

For pest control uses, the sulfur of commerce is usually employed. This is relatively pure, and is prepared for final use by grinding to a small particle size, usually to pass a 300-mesh sieve. The toxicity of sulfur to certain fungi has been shown to be related to its particle size,[34] and there has been a tendency in recent years to use smaller and smaller particles. "Micronized" sulfur, having an average particle size of a few microns, is produced by a special air-attrition process.[38]

Conditioned sulfur is made by adding a small amount of talc, bentonite or other material to prevent caking and to improve the distribution of sulfur dusts. Since sulfur is not easily wetted with water, surface-active agents are frequently added to produce *wettable sulfur*, to be used in sprays. *Flotation sulfur* is produced as a by-product in the manufacture of artificial gas.[32] It has an extremely small particle size (ca. 3 μ) and is usually sold as a paste for spraying purposes.

Sulfur Compounds. Most of the sulfides exhibit fungicidal properties, although the more highly oxidized sulfur compounds, such as the sulfates and thiosulfates, do not.

Lime Sulfur. When calcium hydroxide in water suspension is boiled with sulfur a reaction takes place, resulting in the formation of calcium sulfides, calcium thiosulfate and water. Commercial lime sulfur solution is an orange-red liquid, having a specific gravity of 1.283 (32° Bé). The main reaction products are calcium polysulfides, with the pentasulfide, CaS_5, predominating. Probably the reaction proceeds through several steps, and it is not possible with our present knowledge to write an equation for it.[31]

From the point of view of fungicidal and insecticidal activity, the calcium polysulfides are the most valuable constituents of lime sulfur solutions. When exposed to air, lime sulfur solutions undergo decomposition, and hydrogen sulfide is evolved. Lead arsenate, which is commonly applied with lime sulfur, reacts vigorously with it, producing lead sulfide and liberating soluble arsenic acids which may be phytotoxic. It has been found that the addition of lime and a protective colloid, such as a proteinaceous material like skimmed milk powder, tends to suppress this reaction.[12] This is of considerable practical importance in preventing plant injury when combination insecticide-fungicide sprays are applied. Ferrous sulfate and manganese sulfate have also been used to reduce arsenical injury when lime sulfur-lead arsenate mixtures are applied to plants. These compounds appear to react with the lime sulfur to produce colloidal sulfur, which is less likely to cause injury to plants, although it is a less effective fungicide than the parent compound.

Dry lime sulfur is, as the name implies, the product resulting from the dehydration of liquid lime sulfur. It is much less expensive to transport, but is not as effective a pesticide as the liquid form, probably because the polysulfides are decomposed to a considerable extent in the drying process.[1]

Self-boiled Lime Sulfur. This material is produced without the use of external heat, by utilizing the heat generated by slaking calcium oxide (quicklime) in water to raise the temperature to the point where a reaction takes place between the lime and sulfur. Under these conditions the reaction does not go to completion, and considerable amounts of the original ingredients are present in the final product. For this reason, self-boiled lime sulfur is a milder fungicide than true lime sulfur solution, and is preferred for sensitive plants.

Other inorganic sulfur compounds, including the sulfides and polysulfides of ammonium, barium, potassium and sodium, have been suggested as fungicides, but have not had wide acceptance. Sulfur nitride, S_2N_2, has also been suggested.[5, 15]

Copper Compounds. In addition to sulfur, the other element most widely used as a fungicide is copper. Practically all inorganic compounds of copper are toxic to fungi, and the choice between the various compounds is limited mainly by their physical properties. Copper compounds which are freely soluble are generally too toxic to be used on growing plants: for this purpose an almost insoluble compound is required. Apparently the most efficient copper fungicides are those with a very low solubility, since these permit the slow release of minute amounts of ionic copper.

Bordeaux Mixture. The quasi-accidental discovery by Millardet[25] that the combination of copper sulfate and lime had excellent fungicidal properties, opened up a new era of plant disease control. Soluble copper compounds had been used as fungicides in a limited way prior to this discovery in 1878, but the superior properties of the combination soon led to the wide adoption of this material as a fungicide, and the development of a number of closely related combinations of copper.

Bordeaux mixture is essentially a mixture of lime and copper sulfate. The type of product may be varied by changing the ratio of these two ingredients, but it is usual to use one part of copper sulfate to one or more parts of lime by weight. Originally quicklime (calcium oxide) was slaked and allowed to react with the copper sulfate, but with the advent of highly purified calcium hydroxide, the latter has come into common use. Formulas for Bordeaux mixture are expressed numerically: a 4-4-100 mixture, for example, indicates that 4 pounds of copper sulfate (pentahydrate), 4 pounds of lime, and 100 gallons of water are combined.

The early workers believed that the active material in Bordeaux mixture was copper hydroxide. More accurate chemical investigations, however,[23] have demonstrated that the initial product of the reaction between copper sulfate and calcium hydroxide in an aqueous medium is a basic sulfate of copper, $[Cu(OH)_2]_3CuSO_4$.[28] This compound is formed when less than 0.75 equivalent of calcium hydroxide has been added to one equivalent of copper sulfate. Additional lime causes the decomposition of the basic sulfate, resulting in the formation of a blue hydrated cupric oxide (or hydroxide). The latter compound adsorbs free sulfate ions, forming a complex which is relatively stable.

Properly prepared Bordeaux mixture is a suspension of very finely divided gelatinous particles, having a characteristic light blue color. The physical nature of the precipitate causes it to adhere well to plant surfaces. This is one of the most important and useful characteristics of the fungicide, and one which has not been duplicated in any dried preparation up to the present time. Deposits of Bordeaux mixture upon plant surfaces are resistant to the action of rainfall, dews, etc. It is believed that a reaction takes place between the deposit and the carbon dioxide of the atmosphere and it has been suggested that the resulting product is highly resistant to weathering.

The fungicidal action of Bordeaux mixture is due to the presence of very small amounts of soluble copper. It has been suggested[6, 39] that after carbonation, the deposits subjected to weathering gradually become richer in copper because of the more rapid leaching out of calcium and sulfate, and this change is accompanied by the appearance of increased amounts of soluble copper.

Bordeaux mixtures, as commonly made at present, contain an excess of lime, and hence should not be combined with other pesticides which may be decomposed by alkali. The chlorinated insecticides, pyrethrum, and soaps are materials of this nature.

Materials Related to Bordeaux Mixture. Several mixtures and compounds similar to Bordeaux mixture have been proposed from time to time, and some of them have had considerable practical use. *Burgundy mixture,*[27] or soda Bordeaux, is made by reacting copper sulfate and sodium carbonate. The resulting product is similar in appearance to Bordeaux mixture, but is more likely to cause injury to sensitive plants. For this reason it is seldom used at present. *Eau celeste* is another related material, prepared by adding an excess of ammonium hydroxide to copper sulfate solution.[2] *Eau celeste* is an efficient fungicide, but is readily decomposed, and is apt to cause plant injury. Other cuprammonium mixtures have been suggested, but none has received the wide acceptance accorded Bordeaux mixture, which dominates the field of copper fungicides.

"Fixed Copper" Compounds. While many attempts have been made to prepare a dried Bordeaux mixture, the product usually is inferior, particularly from the point of view of physical properties. Within recent years a variety of "fixed copper" compounds in dry form have appeared on the market. While these usually do not adhere to the plant surfaces as well as Bordeaux mixture, they are efficient fungicides, and the fact that they are convenient to use has led to their wide acceptance.

Most of these materials are basic in nature, and the most common are either basic copper chlorides or sulfates or a combination of the two. These have the general formulas $[Cu(OH)_2]_xCuCl_2$ and $[Cu(OH)_2]_xCuSO_4$; x is usually 3 in the so-called "tribasic" materials. It is likely that the exact composition depends upon the proportion of reactants and the conditions under which they react. Chemically the tribasic sulfates of copper are probably closely related to the compounds formed in Bordeaux mixture. As mentioned earlier, however, the drying process adversely affects the physical properties to a certain extent.

Other "insoluble" copper materials which have found some use as fungicides include copper phosphate, $Cu_3(PO_4)_2$, copper ammonium silicate and copper zeolites. In the latter two substances the copper is held tenaciously by the silicate complexes.

Copper oxide, particularly the cuprous form, is widely used as a fungicide, especially as a seed protectant.[14] It has been demonstrated that for fungicidal uses the particle size of the solid should be as small as possible.[16] A good index of this is the color of the cuprous oxide—the more yellow the material the smaller the particle size. Cuprous oxide is also used as a spray or dust on agricultural crops.

Many copper compounds have been used as fungicides. Mention should be made of basic copper carbonate and copper sulfate: for certain applications these compounds are highly useful. Organic compounds of copper such as copper naphthenate and copper oleate[11] are used widely as preservatives for wood, fabrics, and cordage to prevent fungus attack. Copper 8-quinolinolate is sold for fungicidal use, and is finding some acceptance.[30] Copper oxalate[26] and copper acetate are also used for the control of certain plant diseases.

Apparently the copper ion is highly toxic to all fungi, and is a highly effective fungicide. The main problem in its use is to find a compound which has the proper physical and chemical properties. Bordeaux mixture and the "fixed copper" compounds appear to be the most useful of the group.

Other Inorganic Fungicides. *Mercury Compounds.* Most compounds of mercury are highly toxic to all forms of living matter. Mercuric chloride, $HgCl_2$, has been used as a seed disinfectant and to control fungi attacking certain species of fine grasses used on golf courses, etc. Calomel, Hg_2Cl_2 (mercurous chloride), has also been used for the latter purpose. Mercuric oxide (HgO) is used to treat potato seed pieces. The high toxicity of mercury to higher animals and plants has prevented its general use, although it admittedly is an excellent fungicide.

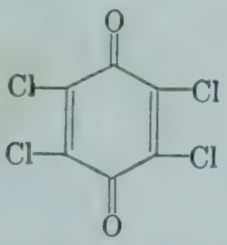
Miscellaneous Inorganic Fungicides. Compounds of most of the heavy metals act as good fungicides, for the most part. At various times compounds of silver,[29] nickel, aluminum, chromium, zinc, and other metals have been suggested as fungicides. Zinc sulfate may be reacted with lime to form a material sometimes called "zinc Bordeaux."[19] Recently complexes containing cadmium, chromium, and other metals have been sold as fungicides for agricultural crops and turf.[8] They appear to be quite satisfactory for certain plant diseases. The tonnage of these miscellaneous chemicals sold, however, is but a small fraction of the copper and sulfur fungicides consumed annually.

ORGANIC FUNGICIDES

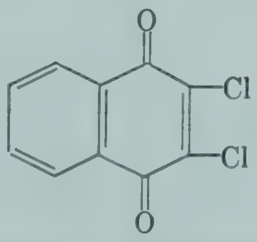
Although the development of synthetic organic chemicals for fungicidal purposes has not proceeded as rapidly as in the insecticide field, a number of organic compounds of considerable potential fungicidal value have been developed.

Organic Mercury Compounds. The highly toxic nature of the inorganic salts of mercury stimulated a search for compounds of the element which would be specifically toxic to lower organisms. A number of organic compounds of mercury have been tested as fungicides,[4] and several of them are widely used to combat fungi which attack germinating seeds. Ethyl mercuric chloride, C_2H_5HgCl, ethyl mercuric iodide, C_2H_5HgI.[21] and ethyl mercuric phosphate are examples of relatively simple compounds of this type. They are used as seed disinfectants. A series of phenyl mercuric derivatives, including hydroxymercurichlorophenol and hydroxymercuricresol, are used for treating vegetable and other seeds. Certain of these are effective against turf diseases as well. Quaternary ammonium compounds containing mercury, such as phenylmercuritriethanol ammonium lactate, are potent fungicides and bactericides.[20]

Chloroquinones. Two compounds, tetrachloro-*p*-benzoquinone (chloranil) and 2,3-dichloro-1,4-naphthoquinone, have proved to be toxic to seed-borne fungi, and are used to prevent damping-off of seedlings.[3, 16] These compounds have the following structures:



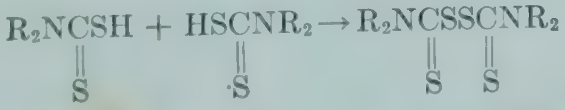
Tetrachloro-*p*-benzoquinone



2,3-Dichloro-1,4-naphthoquinone

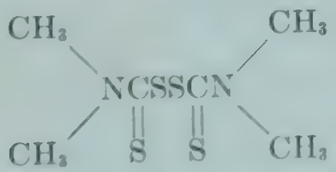
Dithiocarbamates and Thiuram Derivatives. Derivatives of dithiocarbamic acid, $H_2N\underset{\underset{S}{\|}}{C}SH$ have been found to possess considerable fungicidal possibilities. Ferric dimethyl dithiocarbamate (ferbam), zinc dimethyl dithiocarbamate (ziram), disodium ethylene bisdithiocarbamate (nabam) and its zinc salt (zineb) are all available commercially. These compounds are especially useful in combating fungi on crop plants, fruit, and ornamentals.[7, 9, 24, 36]

When dithiocarbamates are oxidized, hydrogen is eliminated and tetraalkyl thiuram disulfides are formed:



$$R_2N\underset{\underset{S}{\|}}{C}SH + HS\underset{\underset{S}{\|}}{C}NR_2 \rightarrow R_2N\underset{\underset{S}{\|}}{C}SS\underset{\underset{S}{\|}}{C}NR_2$$

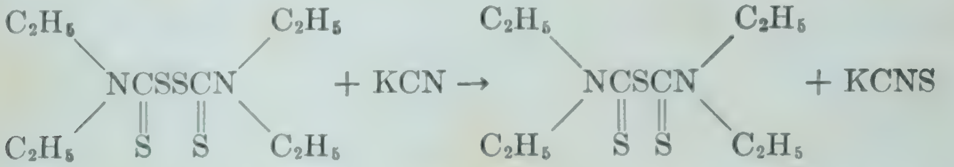
By this means it is possible to prepare tetramethylthiuram disulfide (thiram).



$$(CH_3)_2N\underset{\underset{S}{\|}}{C}SS\underset{\underset{S}{\|}}{C}N(CH_3)_2$$

This is used as a seed treatment, and against turf diseases.

When thiuram disulfides are treated with a sulfur acceptor such as potassium cyanide, thiuram monosulfides are formed:

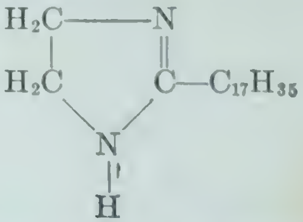


These compounds have not been used as agricultural fungicides to any great extent, but are useful in the treatment of scabies.[7a]

Quaternary Ammonium Derivatives. Compounds having the general formula R_4NX have been found to possess considerable toxicity to lower forms of life, particularly the bacteria and fungi, without being highly toxic to higher animals. A tremendous amount of work has been done on these compounds in recent years,[17] but it has been largely directed toward the medical and sanitation fields, rather than agricultural applications. Most of the quartenary ammonium compounds are water-soluble, which limits their usefulness in outdoor applications, but lauryl isoquinolinium bromide and lauryl nicotinium bromide have been found to be effective as foliage sprays.[18] Quaternary compounds containing mercury have been mentioned earlier.

Nitro- and Heterocyclic Nitrogen Compounds. Several aromatic nitro compounds, such as 4,6-dinitro-*o*-cresol and dinitro-*o*-cyclohexylphenol, are potent fungicides. These compounds have been mentioned earlier as insecticides: they are usually used as dormant or ground sprays against fruit diseases.[33]

Quite recently it has been shown that substituted 2-imidazolines (glyoxalidines) are fungitoxic. One of these, 2-heptadecyl-2-imidazoline, has found application against cherry leaf spot and other fruit diseases.[35, 37]



Miscellaneous Organic Fungicides. Formaldehyde (HCHO) has been used for many years as a seed and soil sterilant. Certain fatty acids, such as propionic acid and its salts, are used to prevent mold and other fungi in baked goods.[13] Pentachlorophenol, Cl_5C_6OH, is used as a wood preservative. It is usually applied in oil solution. Creosote and tar oil fractions have long been used for this purpose.[22]

It is probable that further research will develop new fungicides. Almost certainly they will be organic in nature. Certainly there is much need for improved materials, although the low prices of the standard agricultural fungicides, copper and sulfur, pose many economic problems.

BIBLIOGRAPHY

1. Abbott, W. S., Culver, J. J., and Morgan, W. J., *U. S. Dept. Agr. Bull.* **1371** (1926).
2. Butler, O., *Phytopath.* **7**: 235 (1917).
3. Cunningham, H. S., and Sharvelle, E. G., *Phytopath.* **30**: 4 (1940).
4. Dillon Weston, W. A. R., and Booer, J. R., *J. Agr. Sci.* **25**: 628 (1935).
5. Frear, Donald E. H., "Chemistry of Insecticides, Fungicides and Herbicides." 2nd ed. New York, D. Van Nostrand Co., Inc. (1948).
6. Goldsworthy, M. C., and Green, E. L., *J. Agr. Res.* **52**: 517 (1936).
7. Goldsworthy, M. C., Green, E. L., and Smith, M. A., *J. Agr. Res.* **66**: 277 (1943).

7a. Gordon, R. M., Davey, T. H., Unsworth, K., Hellier, F. F., Parry, S. C., and Alexander, J. R. B., *Brit. Med. J.* **I**: 803 (1944).

8. Harry, J. B., Wellman, R. H., Whaley, F. R., Thurston, H. W., Jr., and Chandler, W. A., *Contrib. Boyce Thompson Inst.* **15**: 195 (1948).
9. Heuberger, J. W., *Plant Disease Reptr., Suppl.* **157**, p. 156 (April 15, 1945).
10. Heuberger, J. W., and Horsfall, J. G., *Phytopath.* **29**: 303 (1939).
11. Hickman, C. J., Marsh, R. W., and Wilkinson, E. H., *Ann. Appl. Biol.* **30**: 179 (1943).
12. Hodgkiss, W. S., Frear, D. E. H., and Worthley, H. N., *J. Econ. Entomol.* **31**: 443 (1938).
13. Hoffman, C., Schweitzer, T. R., and Dalby, G., *Food Res.* **4**: 539 (1939).
14. Horsfall, J. G., *N. Y. (Geneva) Agr. Expt. Sta. Bull.* **615** (1932).
15. Horsfall, J. G., "Fungicides and Their Action." Waltham, Mass., Chronica Botanica Co. (1945).
16. ter Horst, W. P., and Felix, E. L., *Ind. Eng. Chem.* **35**: 1255 (1943).
17. Howard, F. L., *Plant Disease Reptr., Suppl.* **157**, p. 150 (April 15, 1945).
18. Howard, F. L., Keil, H. L., and Mosher, H. H., *Phytopath.* **34**: 1004 (1944).
19. Kadow, K. J., *Trans. Ill. State Hort. Soc.* **68**: 240 (1934).
20. Keil, H. L., *Greenskeeper's Reptr.* **12**(6): 5 (1944).
21. Lammerts, W. E., *Phytopath.* **30**: 334 (1940).
22. Lesser, M. A., *Agr. Chemicals* **11**(2): 22 (1947).
23. Martin, H., *Ann. Appl. Biol.* **19**: 98 (1932).
24. McCallan, S. E. A., *Agr. Chemicals* **1**(7): 15 (1946).
25. Millardet, P., *J. agr. prat.* **49**: 513; 801 (1885).
26. Miller, P. W., *30th Ann. Rept. Oregon State Hort. Soc.* 1938.
27. Mond, R. L., and Heberlein, C., *J. Chem. Soc.* **115**: 908 (1919).
28. Mondain-Monval, P., and Bloy, J., *Compt. rend.* **225**: 122 (1947).
29. Nielsen, L. W., *Cornell Univ. Memoir* **248** (1942).
30. Powell, D., *Phytopath.* **36**: 572 (1946).
31. St. John, J. L., and Groves, K., *Proc. Wash. State Hort. Assoc., 33d Ann. Meeting*, 128 (1938).
32. Sauchelli, V., *Ind. Eng. Chem.* **25**: 363 (1933).
33. Steiner, H. M., *J. Econ. Entomol.* **38**: 117 (1945).

34. Streeter, L. R., and Rankin, W. H., *N. Y. (Geneva) Agr. Expt. Sta. Tech. Bull.* **160** (1930).

35. Thurston, H. W., Jr., Harry, J. B., Lewis, F. H., Groves, A. B., and Taylor, C. F., *Contrib. Boyce Thompson Inst.* **14**: 161 (1946).

36. Tisdale, W. H., and Flenner, A. L., *Ind. Eng. Chem.* **34**: 501 (1942).

37. Wellman, R. H., and McCallan, S. E. A., *Contrib. Boyce Thompson Inst.* **14**: 151 (1946).

38. Wilcoxon, F., and McCallan, S. E. A., *Contrib. Boyce Thompson Inst.* **3**: 509 (1931).

39. Wilcoxon, F., and McCallan, S. E. A., *Contrib. Boyce Thompson Inst.* **9**: 149 (1938).

Chapter XXII

HERBICIDES

Donald E. H. Frear

The Pennsylvania State College, State College, Pa.

Any undesirable plant may be a weed. Many otherwise desirable plants of economic importance may thus become weeds if they are growing in the wrong place or at the wrong time. A good example is grass: in a lawn or pasture, a grass species may be highly desirable; the same grass growing on a tennis court or racetrack may be a weed.

Weeds are of great economic significance in agriculture. They use space, water, and nutrient materials intended for cultivated species, and by their presence reduce the yield of the desirable species. It has been estimated that the annual loss from weeds may be as high as \$3,000,000,000.[20] They affect not only the production of crops, but they may damage or interfere with public utilities, such as power lines, railroad rights-of-way, roads, irrigation canals, etc.

The general methods of weed control parallel those used for insect and plant disease control. Mechanical control measures, particularly cultivation, mowing, flooding, and burning, have been used extensively in the past as weed control measures. Biological methods have had some application and will continue to be employed under certain conditions. Chemical weed control has been practiced for many years on a limited scale, but the advent of a new group of selective herbicides has made this latter method more practicable, and in the light of our present knowledge the field of chemical weed control deserves considerable attention.

Chemical weeds killers are usually classified as *selective* and *nonselective.* Selective herbicides act preferentially on one species or group of plants, and not on another. Nonselective herbicides, on the other hand, kill all types of plant growth indiscriminately. By utilizing some anatomical or physiological characteristic of a plant, it is often possible to make a chemical destroy this plant without harming adjacent plants of different types. A nonselective herbicide may sometimes be made selective by adjusting the concentration of the chemical or time of application. As an illustration, onion plants possess waxy leaves which are not easily wetted by aqueous solutions: for this reason they may not be affected by a spray containing chemicals which will kill weeds growing adjacent to the onions.

The choice of the proper chemical for a specific weed control problem involves many factors, and the improper application to a valuable crop may result in serious financial loss. It is wise, therefore, to make a careful study of each problem, and to be guided by research work and experience applicable to the specific case. Valuable information and advice can be secured readily from local County Agricultural Agents or State Agricultural Experiment Stations.

INORGANIC HERBICIDES

Arsenic Compounds. Arsenic in several chemical combinations is used as a nonselective herbicide. Arsenic pentoxide (As_2O_5) in water solution is sometimes used, but the more common form is "sodium arsenite," made by reacting sodium hydroxide and arsenic trioxide. The product of this reaction is a thick, syrupy liquid, and the concentration is usually designated in pounds of As_2O_3 per gallon of solution. If applied in sufficient concentration, this material will kill all vegetation. Being freely soluble in water, it is readily leached from the soil by rain, and hence loses its effectiveness rapidly if there is an abundant supply of rainfall. By regulating the concentration carefully, arsenic compounds may be used as selective herbicides: crabgrass and other lawn weeds may be killed in this way without permanent damage to desirable grass species.[14, 18]

Boron Compounds. Borax (sodium borate, $Na_2B_4O_7 \cdot 10H_2O$) and colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) have been used as nonselective herbicides, particularly on the Pacific Coast.[5] The cost of these chemicals is relatively low, and they are effective, especially if combined with other herbicides, such as sodium chlorate.

Cyanamide, Cyanides, and Thiocyanates. Calcium cyanamide, $CaCN_2$, may be used either as a nonselective or a selective herbicide. It is frequently applied to soil before crop planting, and used in this way it serves to eradicate weed seeds.[3] Recently it has been used as a defoliant on cotton.[8] On this crop it is desirable to remove the leaves before harvesting the bolls, especially if a mechanical picker is used. A similar application on potatoes, called "artificial frost," is used to remove growing portions of the plant before digging. Calcium cyanide contains both calcium and nitrogen, and thus has considerable fertilizer value. It decomposes in the presence of water to yield cyanamide:

$$CaCN_2 + 2H_2O \rightarrow H_2CN_2 + Ca(OH)_2$$

Ammonium thiocyanate, NH_4SCN, is available in considerable quantities as a by-product of the artificial gas industry, and is finding considerable use as a herbicide. It is readily soluble in water, and forms an odorless solution which is highly toxic to plants. Solutions of ammonium thiocyanate are corrosive to metals, but are relatively nontoxic to man and animals.[13] Sodium and calcium thiocyanates have properties similar to the ammonium salt. Potassium cyanate, KOCN, has recently been used as a weed killer in the same general way as the thiocyanates. Like calcium cyanamide, the thiocyanates and cyanates add nitrogen to the soil.

Chlorates. One of the more extensively used herbicidal chemicals is sodium chlorate, $NaClO_3$.[13] This is freely soluble in water, and is highly toxic to all plants. Its main use is as a nonselective herbicide and soil sterilizing agent. It has been found that the physical properties of the soil determine to a considerable extent how prolonged the herbicidal action of sodium chlorate will be.[10]

Sodium chlorate is a powerful oxidizing agent, and when in contact with organic matter may ignite spontaneously. This property makes the compound dangerous to use: many fires have been caused by spilling sodium chlorate solutions on clothing, shoes, etc. Any solution accidentally spilled on combustible material should be washed off immediately before it dries. Sodium chlorate is frequently diluted with other chemicals to reduce the fire hazard, and some of these combinations are relatively safe.

Sulfamates. Sulfamic acid, H_2NSO_3H, and its ammonium salt, $H_2NSO_3NH_4$, have herbicidal properties. The latter is frequently used against poison ivy. It is freely soluble in water, and is usually applied in solution. It is not highly toxic to animals, and is not hazardous to use. At sufficiently high concentrations, ammonium sufamate acts as a soil sterilant.

Sulfuric Acid. Although any acid is a potential herbicide, the cost of many of them prohibits their use. Sulfuric acid, technical grade, is relatively cheap, and it has been used extensively as a herbicide. In sufficient concentration, sulfuric acid will destroy all living matter. By suitable regulation of the concentration, however, it is possible to destroy weeds in cereal crops without reducing the yield of grain.[2] It is perhaps used more frequently in Europe than in this country.

Solutions of sulfuric acid are corrosive, and resistant equipment should be used wherever possible. In any but the lowest concentrations it is toxic to man and animals, and care should be exercised in mixing and application. For safety, concentrated acid should always be added to large volumes of water in making dilute solutions: adding water to concentrated acid may lead to disastrous consequences.

Miscellaneous Inorganic Herbicides. One of the most common inorganic herbicidal chemicals is salt, NaCl. Killing plants by plasmolysis, salt is effective if applied in sufficient quantities. It is particularly useful to keep weeds and grass from growing on walks, drives, tennis courts, and similar hard-surfaced areas. Calcium chloride is also used for the same purpose. Compounds of copper, especially copper sulfate and nitrate,[13] have been used to eradicate weeds in cereal crops. Concentrations below 2 per cent act as selective herbicides for this purpose. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) is a selective weed killer, and is often used to destroy broad-leaf weeds in lawns. It is comparatively low in cost and may be applied in solution or as a dry powder.[7] Certain fertilizer materials, such as ammonium nitrate and potassium chloride, may be used to destroy vegetation if applied in sufficient concentration. Such materials may be used to advantage to destroy weeds on fallow ground shortly before planting time.

ORGANIC HERBICIDES

Oils. Crude petroleum oil and most of the commercial petroleum fractions are toxic to plants if applied in high enough concentration (see Chapter XX). In some areas, crude oil is used to keep down weeds along railroad tracks. Lighter fractions, including kerosene, Stoddard solvent, and naphtha, are used for specific applications.[6] Certain plants are apparently quite resistant to these oils, and carrots, for example, may be freed from weeds without injury by a thorough spraying with a light petroleum oil.[16]

Nitro Compounds. Various organic nitro derivatives are phytotoxic. Some of these compounds are useful in low concentrations as fungicides and insecticides, and have been discussed in the two preceding chapters. By increasing the concentration, it is possible to utilize these materials as herbicides. One of the most commonly used of these is 4,6-dinitro-*o*-cresol. This compound or its water-soluble sodium salt, frequently can be used either as selective or nonselective herbicides.[19] For eradicating weeds in legume forage crops, concentrations of approximately 0.25 per cent appear to be effective without injuring the desirable crop species.

Sodium dinitro-*o*-cresylate is inflammable in its dry form, and is usually sold as a concentrated water solution or suspension. Although it is a good dye, and apt to stain clothing, it has few other disadvantages: it is not highly toxic, and is comparatively inexpensive to use. A related compound, 2,4-dinitro-6-*sec*-butyl phenol,[4] has been found to be highly phytotoxic. The corresponding *sec* amyl derivative is also commercially available for herbicidal use. These compounds are soluble in petroleum oil, and are applied as oil solutions.

Chlorinated Compounds. Pentachlorophenol, Cl_5C_6OH, is an inexpensive chemical which has recently been widely used as a herbicide. Made by the exhaustive chlorination of phenol, the crude reaction product contains approximately 80 per cent of pentachlorophenol, with the balance other chlorinated phenols. This material is applied as an oil solution; the sodium salt is water-soluble, and is used in the same way, dissolved in water.[9]

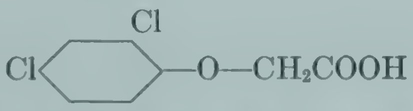
Sodium trichloroacetate (TCA), which has the formula $Cl_3CCOONa$, has recently been used for specific herbicidal applications. It is highly toxic to certain species of grass, notably quack grass and Johnson grass. The compound is readily soluble in water, and is applied at the rate of 75–150 pounds per acre for complete eradication of these grasses.

Mercury Compounds. Several compounds containing mercury have showed promise as selective herbicidies and seem to be especially valuable in eradicating crab grass, a serious pest in fine lawns. Phenyl mercuric acetate (PMAS) and phenyl mercuric ethanol ammonium lactate are now available commercially.

2,4–D Compounds. It has been known for a number of years that certain oxy derivatives of cyclic organic compounds functioned as plant hormones. (See Chapter XIII, Volume I.) Within the past few years some of these compounds have been developed as selective herbicides, and they have been widely accepted.[1, 11]

It has been said that the 2,4–D herbicides have revolutionized American agriculture. Although this statement may not be entirely true, few would gainsay the fact that these chemicals have had a profound effect on crop production in this country. Compounds of the 2,4–D group are truly selective herbicides: in general they kill the broad-leafed plants, and are relatively harmless to the monocotyledonous plants. Since the latter group includes the highly important grasses and cereals, it may be seen that practically every farmer can find use for 2,4–D in one form or another.

Chemically, 2,4–D is 2,4-dichlorophenoxyacetic acid.



The free acid is a white crystalline solid, only slightly soluble in water. The salts of the acid, notably the sodium, ammonium, and organic amine salts, however, are water-soluble, and may be applied as dilute solutions. The esters of the acid are insoluble in water, and must be applied as emulsions or as solutions in organic solvents. Each of these types has certain special properties, and will be discussed below.

2,4–D Acid is rarely used in its original form as a herbicide because of its low solubility. Mixtures of the acid with an alkaline material such as sodium carbonate were marketed in the dry form at one time. When mixed with water, the two chemicals reacted to form sodium 2,4-dichlorophenoxyacetate, which was freely soluble. Since the sodium salt is now available, the free acid is now rarely used, except for manufacturing purposes.

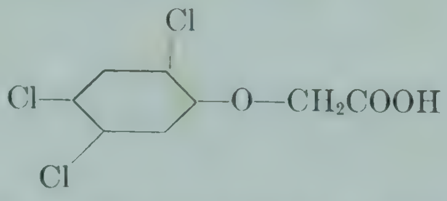
2,4–D Sodium Salt. As mentioned above, this compound is soluble in water to a limited extent, and, since only minute concentrations are sufficient to be phytotoxic, a water solution of this substance is convenient for many applications. Being a dry powder, this form is economical to transport and store. Within recent years, however, there has been a tendency to apply 2,4–D in relatively concentrated form, since this obviates the necessity for large volumes of water, with the attendant problems of transportation in the field. The solubility of the sodium salt is so low that it is impossible to make solutions containing more than 10 per cent in water: this rules out this compound if low-volume spraying is practiced. If large-volume spraying is done, using 50–100 gallons of spray per acre, the sodium salt is still frequently used. Golf courses, athletic fields, etc., are in many cases treated with this form.

2,4–D Amine Salts. The search for salts of 2,4–dichlorophenoxyacetic acid which would be freely soluble in water led to the development of the organic amine salt formulations. The aliphatic amines are generally strongly basic, and readily combine with acids to form salts. Various amines have been combined with 2,4–dichlorophenoxyacetic acid, including mono-, di- and triethyl amines, mono, di- and triethanolamines, and mono- and tri-isopropylamines. The resulting salts are all liquids, and are water-soluble. Being more soluble than the sodium salt, they can be made into concentrated solutions, thus lending themselves to low-volume applications mentioned above. With modern spray nozzles it is possible to apply as little as 2 or 3 gallons of spray evenly over an acre of ground, and for this a relatively concentrated solution is required. Being liquids, the amine salts of 2,4–D do not clog the small orfices of the small-volume nozzles, and are preferred by many operators.

The salts of 2,4–D are essentially nonvolatile. This is an advantage for certain applications, for where sensitive crops are growing near sprayed fields, volatile 2,4–D forms often cause injury at a distance (see next paragraph).

2,4–D Esters. Like all organic acids, 2,4–dichlorophenoxyacetic acid readily forms esters with alcohols. A number of esters of 2,4–D are now available, including the methyl, ethyl, isopropyl, butyl, and butoxy ethanol forms. Like the amine salts, these are liquids. They differ, however, in being insoluble in water, and are usually dissolved in an organic solvent, and emulsified for final application. Since they are liquids they offer the same mechanical advantages as the amine salts. However, they have appreciable vapor pressures, and consequently are somewhat volatile. As mentioned previously, this is a disadvantage if there are sensitive plants adjacent to sprayed areas. Severe damage to neighboring crops has resulted from this property of the ester formulations. It is generally believed that the esters of 2,4–D are slightly more active physiologically than the salt forms, although this has been disputed.

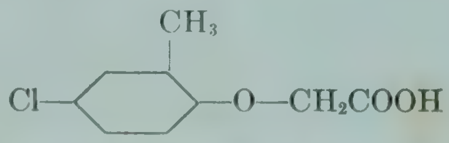
2,4,5-Trichlorophenoxyacteic Acid (2,4,5–T). The introduction of a third chlorine atom into the 2,4–D molecule apparently increases the phytotoxicity of the material. Formulations of 2,4,5–T are recommended for killing resistant plants, particularly brush, brambles and herbaceous plants generally.



The free acid, amine and esters forms of 2,4,5–T are available commercially: they have chemical and physical properties similar to the corresponding 2,4–D formulations.

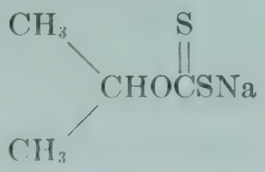
Combinations of 2,4–D and 2,4,5–T are available, both for general herbicidal applications and brush killing.

Related Compounds. In England, a compound related to 2,4–D, 2-methyl-4-chlorophenoxyacetic acid,

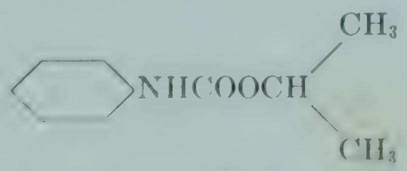


is used as a herbicide. This is chemically quite similar to 2,4–D, and apparently possesses much the same physiological properties.[17] Other compounds closely related to 2,4–D have been tested as herbicides, but insufficient data are available at present to permit proper evaluation.

Miscellaneous Organic Herbicides. Two compounds should be mentioned in this category. Both have received considerable attention, but neither has been widely adopted. The first is sodium isopropyl xanthate



and the other is isopropyl N-phenyl carbamate[12]



Perhaps further work on these compounds will demonstrate their usefulness. Many other organic compounds have been suggested as herbicides, but none appears to be outstanding at present.

BIBLIOGRAPHY

Literature Citations

1. Akamine, E. K., *Univ. Hawaii Agr. Expt. Sta. Circ.* **26** (1948).
2. Ball, W. E., and French, O. C., *Calif. Agr. Expt. Sta. Bull.* **596** (1935).
3. Clayton, E. E., Gaines, J. G., Smith, T. E., and Graham, T. W., *Phytopath.* **35**: 483 (1945).
4. Crafts, A. S., *Science* **101**: 417 (1945).
5. Crafts, A. S., and Raynor, R. N., *Hilgardia* **10**: 343 (1936).
6. Crafts, A. S., and Reiber, H. G., *Hilgardia* **18**: 77 (1948).
7. Dawson, R. B., *Sci. Hort.* **5**: 167 (1937).
8. Gull, P. W., and Dunnam, E. W., *Agr. Chemicals* **2**(6): 33 (1947).
9. Hirsch, A. A., *Bot. Gaz.* **103**: 620 (1942).
10. Hurd-Karrer, A. M., *J. Agr. Research* **63**: 481 (1941).
11. Kraus, E. J., and Mitchell, J. W., *Bot. Gaz.* **108**: 301 (1947).
12. Lachman, W. H., *Proc. Am. Soc. Hort. Sci.* **51**: 541 (1948).
13. Robbins, W. W., Crafts, A. S., and Raynor, R. N., "Weed Control." New York, McGraw-Hill Book Co., Inc. (1942).
14. Runyan, C. R., *Turf Culture* **1**: 61 (1939).
15. Silversides, W. H., *Sci. Agr.* **20**: 419 (1940).
16. Sweet, R. D., Raleigh, G. J., and Kunkel, R., *Food Packer* **25**(12): 43 (1944).
17. Tincker, M. A. H., *J. Roy. Hort. Soc.* **71**: 141 (1946).
18. Welton, F. A., and Carroll, J. C., *J. Am. Soc. Agron.* **30**: 816 (1938).
19. Westgate, W. A., and Raynor, R. N., *Calif. Agr. Expt. Sta. Bull.* **634** (1940).
20. Wilson, H. K., *Bot. Rev.* **10**: 279 (1944).

General References

21. Cook, W. H., and Halferdahl, A. C., *Natl. Res. Council Canada Bull.* **18** (1937).
22. Frear, D. E. H., "Chemistry of Insecticides, Fungicides and Herbicides." New York, D. Van Nostrand Co., Inc. (1948).
23. Frear, D. E. H., "Pesticide Handbook." State College, Pa., Commercial Printing Inc. (1951).
24. Heal, R. R., and Thompson, D. G., "Bibliographical Report on Herbicides." St. Paul, Minn., Univ. Minn. Campus Book Store (1949).
25. Robbins, W. W., Crafts, A. S., and Raynor, R. N., "Weed Control." New York, McGraw-Hill Book Co., Inc. (1942).

PART V

COMMERCIAL AGRICULTURAL CHEMISTRY

Chapter XXIII

INVENTIONS AND PATENTS RELATING TO AGRICULTURAL CHEMISTRY

Charles W. Rivise and Abraham D. Caesar

Caesar and Rivise, Philadelphia, Pa.

The development of an invention to the commercial stage, particularly in the field of agricultural chemistry, involves the expenditure of considerable time, effort, and money. The results would in many instances not justify the expense were it possible for those who did not share in the expense to avail themselves freely of the new development. It is, therefore, very important for all those engaged in research or who are likely to make inventions to consider how they can best protect and safeguard their mental creations.

There are two ways, and only two, in which an organization which intends to commercialize its new developments can prevent its competitors from copying or imitating its products. One is by practicing the inventions as trade secrets, and the other is by means of a patent. These two methods are wholly inconsistent. Trade secrets depend upon keeping the details out of the hands of competitors, whereas to obtain patent protection the inventor must make a full disclosure of his invention. Hence, a choice must be made in the case of each invention.

In making a choice between trade secrets and patents, it is important to bear in mind that it is not a simple choice between two extremes. It is rarely possible to obtain absolute secrecy or to secure an absolute patent monopoly. Hence, the choice resolves itself down to balancing advantages and disadvantages and to considering relative risks.

Not all new developments can be protected as trade secrets. Physical devices can rarely be kept secret, and few chemical products defy analysis or cannot be forced to give some indication of the process by which they were made. Neither can all inventions or discoveries be patented. As we shall see, patent protection is restricted to certain categories and must fulfill certain conditions.

One of the strictest requirements for patent protection is that the new development must involve invention or originality. Where the presence of invention is clear, patent protection has the edge over trade secrets. In cases of doubt, it may be advisable to endeavor to obtain patent protection while keeping the invention secret. If the effort to get a patent fails, the practice of the process can be continued as a trade secret, it being remembered that the secret can only be enforced against those who learn its details by fraudulent means or a violation of confidence.

Patent Office Classification of Inventions

The Patent Office has subdivided the entire field of patentable invention into over 350 classes, each one of which is further subdivided into subclasses.

The following classes include most of the inventions in agricultural and related fields except those for designs:

Class	*Subject Matter*
6	Bee Culture
17	Butchering
21	Preserving, Disinfecting, and Sterilizing
23	Chemistry
31	Dairy
43	Fishing, Trapping and Vermin, Destroying
47	Plant Husbandry
54	Harness
55	Harrows and Diggers
56	Harvesters
71	Chemistry—Fertilizers
99	Foods and Beverages
111	Planting
119	Animal Husbandry
127	Sugar, Starch, and Carbohydrates
130	Threshing
131	Tobacco
146	Vegetable and Meat Cutters, and Comminuters
167	Medicine, Poisons, and Cosmetics
168	Farriery
195	Chemistry—Fermentations
252	Compositions
256	Fences
260	Chemistry—Carbon Compounds
275	Scattering Unloaders

Prerequisites of Patentability

Patent protection is based upon a provision in the Federal Constitution, and upon certain statutes passed by Congress. The inventor, in order to take advantage of these statutes, must comply with certain requirements. Furthermore, the alleged invention or discovery must fulfill certain essential conditions. These requirements and conditions will be defined and explained for the most part by means of examples taken from litigated patents. Wherever possible, the examples will be limited to industries involving the field of agriculture and related industries.

Patentable Subject Matter. The first prerequisite for patentability is that the invention must be directed to patentable subject matter. This means that the invention must be capable of being expressed in at least one of the following ways:

1. An art;
2. A machine;
3. A manufacture;
4. A composition of matter;
5. An improvement on any of the foregoing;
6. Variety of plant, other than a tuber-propagated plant, capable of being asexually reproduced; and
7. A design for an article of manufacture.

The foregoing classification is purely statutory, and limits the protection of the patent law to definite lines of activity. Each of the terms has been so defined by patent tribunals as further to limit the field of patentable invention. All other contributions are not patentable, regardless of how valuable to mankind they may be.

It is noted that patents covering the first five categories are sometimes referred to as "utility patents," because their subject matter must possess utility. Design inventions need not possess utility but instead must possess esthetic appeal. Plant inventions need not possess either utility or esthetic appeal.

Art or Method. The term "art" is commonly considered synonymous with the words "process," "method," and "mode of treatment." It may best be defined as "an operation or series of operations performed by rule to produce a given result."

Patentable processes may be roughly classified into (1) chemical processes, and (2) mechanical methods.

As examples of chemical processes may be mentioned:

1. A method of killing weeds by means of alkaline earth chlorides and salt held patentable in *Chipman Chemical Engineering Co. Inc. v. Reade Mfg. Co. Inc.*, 56 F. 2d. 1048 (D.N.J. 1932); affirmed 62 F. 2d. 430 (C.C.A. 3, 1932).

2. A method of killing insects with DDT, held patentable in *Ex parte Müller,* 81 U.S.P.Q. 261 (B.A. 1947).

3. Method of cleaning and bleaching nuts, which consists in dipping the nuts into a solution containing sal soda and chloride of lime. Patent No. 663,069 sustained in *Fullerton Walnut Growers' Ass'n v. Anderson-Barn-Grover Mfg. Co.*, 166 F. 443 (C.C.A. 9, 1908).

4. Method of making arsenate of lead disclosed in Patent No. 892,603, held valid in *Toledo Rex Spray Co. v. California Spray Chemical Co.*, 268 F. 201 (C.C.A. 6, 1920).

5. Method of making mushroom spawn disclosed in Patent No. 1,869,517. *Pennsylvania Research Corp. v. Lescarboura Spawn Co.*, 42 U.S.P.Q. 375 (E.D. Pa. 1939).

6. Method of producing a homogeneous composite of cream and Roquefort cheese. *Sharpless Co. v. Crawford Farms*, 1923 C. D. 554 (C.C.A.2, 1923).

The following are a few representative examples of mechanical methods:

1. Method of operating a mammoth incubator. Patent No. 1,911,250 sustained in *Cugley v. Bundy Incubator Co.*, 93 F. 2d. 932 (C.C.A. 6, 1937).

2. Method of bolting flour disclosed in Reissue Patent No. 5,841, upheld in *Cochrane v. Deener*, 1877 C.D. 242 (S.Ct. 1877).

3. Methods of surgical treatment of trees to prevent decay. Patents Nos. 890,968 and 958,478 held valid in *Darey Tree Expert Co. v. Van Billiard*, 261 F. 996 (C.C.A. 3, 1919).

It is important to note that a mechanical process to be patentable must not be merely the obvious, inherent, or necessary mode of operation of a machine. In other words, the function or operative effect of a machine is not patentable. The usual test is whether the process can be carried out by hand or by more than one form of machine or tool.

In *Chisholm-Ryder Co. Inc. v. Buck*, 65 F. 2d. 735 (C.C.A. 4, 1933), Patent No. 1,256,491 for a method of snipping string beans was held invalid because the method could not be carried out by more than one form of machine. In *Waxham v. Smith*, 294 U. S. 20 (S.Ct. 1935), the Supreme Court refused to invalidate Patent No. 1,262,860 for a method of incubating eggs, because it appeared that the method was not merely the obvious, inherent, or necessary mode of operation of one form of incubator.*

Processes involving mental operations are generally unpatentable. As an example may be mentioned a method of figuring the amount of a given weedkiller necessary to destroy the weeds on a field of given acreage.

Machine. The term "machine" may be defined as an assemblage or combination of mechanical or electrical elements or both adapted to receive, transmit, and modify force or motion to do work.

The following are a few illustrations:

1. Feather picking apparatus for fowls. Patent No. 2,300,157 sustained in *Campbell et al. v. Mueller et al.*, 159 F. 2d. 803 (C.C.A. 6, 1947).

2. Device for extracting juice from fruits and vegetables disclosed in Patent No. 2,273,093. *Modern Products Supply Co. v. Drachenberg*, 152 F. 2d. 203 (C.C.A. 6, 1945).

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* This patent was later held invalid for another reason. *Smith v. Hall et al.*, 33 U.S.P.Q. 249 (S.Ct. 1937).

3. Apparatus for handling eggs and for cleaning and coating them with mineral oil preparatory for shipment or cold storage. Patent No. 1,489,944 litigated in *Nye & Nissen v. Kasser Egg Process Co.*, 96 F. 2d. 420 (C.C.A. 9, 1938).

4. The harvester disclosed in Olin Patent No. 283,812 held valid in *Deering v. Winona Harvester Works*, 155 U. S. 286 (S.Ct. 1894).

5. The grain binder disclosed in Stewart Patent No. 272,598. Ibidem.

6. Peach-peeling machine disclosed in Patent No. 1,104,175. The peaches were subjected to a bath in a hot lye solution to disintegrate the skin, and then passed between rotary brushes and jets of water to wash off the skin. *Dunkley Co. v. Central California Canneries*, 7 F. 2d. 972 (C.C.A. 9, 1925).

Manufactures. The term "manufacture" is synonymous with "article," or "article of manufacture," and includes everything that is made by the art or industry of man, except machines, compositions, and designs.

The following are several representative examples:

1. Barbed wire fence for keeping cattle from straying disclosed in Glidden Patent No. 157,124, held valid in *Washburn & Moen Mfg. Co. v. Beat Em Barbed Wire Co.*, 143 U. S. 275 (S.Ct. 1892).

2. The insoluble capsule for killing tape worms in fowls disclosed in Lee Patent No. 1,778,264 sustained in *George H. Lee Co. v. Pratt Food Co.*, 71 F. 2d. 823 (C.C.A. 3, 1934).

3. Egg flat or holder disclosed in Patent No. 1,429,207, and upheld in *Patent Royalties Corp. v. Land O'Lakes Creameries*, 89 F. 2d. 624 (C.C.A. 2, 1937).

4. Holder or dispenser for insect poison disclosed in McIvor Patent No. 2,082,712. This patent was invalidated in *McIvor v. Chemurgic Corp.*, 104 F. 2d. 58 (C.C.A. 9, 1939).

5. Fowl's mask or blinder to prevent cannibalism disclosed in Cridlebaugh Patent No. 2,079,107, and held lacking in invention in *Cridlebaugh v. Rudolph*, 131 F. 2d. 795 (C.C.A. 3, 1942).

6. Guard for cow stalls disclosed in Patent No. 1,215,569. *Humane Stanchion Works v. Mitchell Mfg. Co.*, 23 F. 2d. 5 (C.C.A. 7, 1928).

Building and parts of buildings come within the term "manufacture." In *William H. Lutton Co. v. Lord & Burnham Co.*, 16 F. 2d. 490 (S.D. N.Y. 1926),[*] Patent No. 1,210,502 for a greenhouse construction was sustained. Likewise in *Lantz et al. v. Morris et al.*, 33 F. 2d. 283 (C.C.A. 8, 1929), Patent No. 1,590,982 covering a farrowing house for sows and their young pigs was held valid. Reissue Patent No. 22,221 for an air-conditioned tobacco barn was sustained in *Florence-Mayo Nuway Co. v. Hardy*, 77 U.S.P.Q. 439 (C.C.A.4, 1948).

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[*] This decision was affirmed in 19 F. 2d. 1023 (C.C.A. 2, 1927).

Composition of Matter. A "composition of matter" may be defined as that which is formed by intermixing or reacting two or more substances. A composition in the sense of the patent law may be a chemical union or a mechanical mixture, and may consist of fluids, solids, or gases.

As examples of compositions may be mentioned a definite chemical compound such as calcium chloride, carbolic acid, 2,4–D, DDT, etc., a synthetic resin, pharmaceutical, paint, insecticide, herbicide, dye, etc.

As another example of a composition may be mentioned the mushroom spawn disclosed in Patent No. 1,869,517 which was sustained in *Pennsylvania Research Corp. v. Lescarboura Spawn Co.*, 42 U.S.P.Q. 375 (E.D. Pa. 1939). The spawn consisted of a cereal substrate overgrown with mycelium.

As another example may be mentioned the jelly-making product of concentrated pectin disclosed in Patents Nos. 1,082,682 and 1,304,166. *Douglas Pectin Corp. v. Armour & Co.*, 27 F. 2d. 814 (C.C.A. 2, 1928).

There has been some agitation against granting patents on newly invented chemical compounds. In *Schering Corp. v. Gilbert*, 68 U.S.P.Q. 84 (C.C.A. 2, 1946), the dissenting judge contended that a claim for a new compound covered merely a chemical formula or a principle of nature.

An article may be composed in whole or in part of one or more compositions of matter, some or all of which may meet the requirements of patentability. Patent No. 1,752,917 covers both a composition consisting of bitumen intermixed with organic and inorganic fibers, and a storage battery container made of the composition. The patent was sustained in *National Battery Co. v. Richardson Co.*, 17 U.S.P.Q. 60 (C.C.A. 6, 1933).

For convenience, the term "product" is very often used to include both articles and compositions.

Improvements. An improvement is an addition to or an alteration in some largely existing art, machine, manufacture, or composition. It need not be better in all respects than the thing upon which it purports to be an improvement. In the present state of the arts most of the inventions for which patents are being granted are but improvements on some prior invention. However, the day of generic or basic patents is not yet past. The improvement may or may not constitute an infringement on the invention on which it is an improvement.

An excellent example of a patentable improvement is the process of separating moisture from milk covered by Merrell Patent No. 860,929. It was old to spray the milk in its natural form through a current of hot air. Merrell found that by first heating the milk in a vacuum pan to evaporate part of the moisture, the danger of injury to the milk was greatly reduced and the product kept much better. The patent was sustained in *Merrell-Soule Co. v. Northland Dairy Co.*, 28 F. 2d. 924 (C.C.A. 6, 1928).

Varieties of Plants. The statutes were amended in 1931 to extend patent protection to the work of men who, like the late Burbank, created or discovered new varieties of plants. As was held in *In re Arzberger*, 46 U.S.P.Q. 32 (C.C.P.A. 1940), Congress in amending the law intended to benefit agriculturalists and horticulturists and to remove the existing discrimination between plant developers and industrial inventors.

The patent statutes specifically provide that a patent may be obtained by any person who has invented or discovered and *asexually reproduced any distinct and new variety of plant, other than a tuber-propagated* plant. The law does not require that plants to be patentable be either useful or ornamental.

In re Arzberger, supra, held that the term "plant" in the law is used in a popular and not scientific sense, and hence does not include bacteria, which are scientifically classified as plants.

Plant patents are classified in the Patent Office in Class 47—Plant Husbandry.

Designs. A design may be defined as that which gives a peculiar or distinctive appearance to an article of manufacture. The appearance may be the result of peculiarity of configuration, or of ornament alone, or of both conjointly.

Formerly, design patents were not granted on devices having mechanical utility, but within recent years many patents have been granted on articles and machines having only mechanical utility.

Unpatentable Inventions and Discoveries. Certain inventions and discoveries are not patentable, irrespective of how much ingenuity was exercised by the inventor or discoverer and regardless of how much they served to advance the arts and sciences. As examples may be mentioned abstract discoveries, certain types of products and new uses of old substances. Under the recently enacted Atomic Energy Act, inventions or discoveries which are useful solely in the production or utilization of fissionable material or atomic energy for military weapons are no longer patentable.

Abstract Discoveries. It is noted that the list of patentable subject matter does not include abstract forces of nature, causes, and effects.

In the recent case of *Katz v. Horni Signal Mfg. Co.*, 63 U.S.P.Q. 190 (C.C.A. 2, 1944) the court stated:

> "Epoch-making 'discoveries' of 'mere' general scientific 'laws,' without more, cannot be patented. So the great 'discoveries' of Newton or Faraday could not have been rewarded with such a grant of monopoly. . . ."

To the examples given in the quotation may be added the following:

1. The discovery that ether would produce insensibility to pain in animals and human beings. *Morton v. New York Eye Infirmary Co.*, 5 Blatchford 116 (D. N.Y. 1862).

2. The discovery that the old process of fumigating plants and trees by hydrocyanic gas could be carried on more effectively at night due to the absence of the actinic rays of the sun. *Wall v. Leck*, 66 F. 552 (C.C.A. 9, 1895).

3. The discovery that certain strains of root-nodule bacteria do not exert a mutually inhibitive effect on each other. *Funk Brothers Seed Co. v. Kalo Inoculant Co.*, 76 U.S.P.Q. 280 (S.Ct. 1948).

4. The discovery that it is the gamma isomer of benzene hexachloride which is the effective toxicant in an insecticide containing a mixture of the isomers. *In re Thomas*, 630 O.G. 1095 (C.C.P.A. 1949).

It is very important to bear in mind that, although neither the cause nor its effect is patentable as such, the means by which the cause is applied to produce the effect may be patentable. Likewise, a new property in matter, when practically applied in the making of a new product, may be the basis of a valid patent. In other words, the principle of nature itself is not patentable, but its utilization by means of an art, machine, manufacture, or composition of matter, when properly expressed in one of these forms, is patentable.

For instance, in *Tilghman v. Proctor,* 102 U. S. 707 (S.Ct. 1881), Patent No. 11,766 for a process of making fatty acids and glycerin was held valid, although it was based on the principle that fats can be broken down into fatty acids and glycerin by heating with water at high temperatures and pressures. And in *Guaranty Trust Co. v. Union Solvents Corp.*, 61 F. 2d. 1041 (C.C.A. 3, 1932), Patent No. 1,315,585 to Weizman for a method of producing alcohol by fermentation was held valid, although it depended upon the life processes of certain bacteria.

Unpatentable Products. The product of a process is not an article in a patent sense, unless it has been transformed from raw or prepared materials in such a manner as to acquire a new or distinctive form, quality, or property.

The following are examples of things which were held not to be patentable products:

1. Pear with inedible portion removed. *In re Ewald*, 54 U.S.P.Q. 82 (C.C.P.A. 1942).

2. Fruit, whose skin had been treated with borax to prevent decay. *American Growers Case,* 1931 C.D. 711 (S.Ct. 1931).

3. Alcoholic extract of odoriferous glands of muskrat. *Ex parte Sparhawk,* 64 U.S.P.Q. 339 (B.A. 1944).

Takamine Patent No. 730,176 for the purified blood pressure raising principle of the suprarenal glands of animals was held valid, because it was a new thing commercially and therapeutically. *Parke-Davis case,* 189 F. 95 (S.D.N.Y. 1911).

Products of nature are not patentable unless they qualify as botanical plants.

New Uses. The list of patentable subject matters does not include new uses, but for many years patents were granted on what appeared to be mere uses of old products. Recently, *In re Thuau,* 57 U.S.P.Q. 324 (C.C.P.A. 1943) reversed this practice, but this does not mean that protection is precluded in all cases.

An employee of the Department of Agriculture discovered that pure gamma,gamma-dipyridyl was an excellent insecticide. A claim for this compound as an insecticide was refused *In re Smith,* 65 U.S.P.Q. 167 (C.C.P.A. 1945). He might have gotten a claim to a method for killing insects using this compound. In fact Müller got a claim for an insecticide containing DDT and certain types of vehicles (Reissue Patent No. 22,922).

Jones invented two new chemical compounds, naphthyl methyl thiocyanate and naphthyl methyl isothiocyanate, and discovered that they were useful as plant regulating compositions, insecticides, and fungicides. He was allowed claims covering the two substances as compounds, but was refused claims for their uses. *In re Jones,* 65 U.S.P.Q. 480 (C.C.P.A. 1945).

In *In re Haller,* 73 U.S.P.Q. 403 (C.C.P.A. 1947), an unsuccessful attempt was made to avoid the rule against use patents by defining the material of the invention as "a package product comprising . . . labeled to show its use as an insecticide."

Utility. The second prerequisite for all inventions except designs and plants is that the invention must possess utility.

An invention to have utility must not only have a good and useful purpose, but it must also be capable of accomplishing its intended purpose.

A method of artificially spotting tobacco leaves was held unpatentable, because the purpose of the invention was to deceive the public into thinking that the spots were natural. *Rickard v. Du Bon,* 103 F. 868 (C.C.A. 2, 1900).

A toothpaste said to be capable of rebuilding the teeth was held unpatentable, because it could not accomplish the intended result. *Hoover case,* 16 U.S.P.Q. 327 (C.C.A. 3, 1933).

The foregoing cases should be compared with *Naylor v. Alsop Process Co.,* 168 F. 911 (C.C.A. 8, 1909), and *Berlin Mills Co. v. Procter & Gamble*

Co., 254 U. S. 156 (S.Ct. 1920). In the first case, a method of bleaching flour was held patentable, although there was evidence that the process had been used to palm off on the public flour made from inferior grades of wheat. It was shown, however, that the process prepared the flour for immediate use in the domestic arts and eliminated the expense of storage. Furthermore, whiteness is as desirable in flour as yellowness in butter and whiteness in sugar. In the second case, the Supreme Court overruled the defense that a patent for a lard substitute should be held void because it might be used to defraud people who wanted genuine lard. The Court stated that the invention had brought an excellent food material similar to lard within the reach of the poorer classes. The patent was, however, invalidated for other reasons.

Novelty. The third requirement for patentability is that the device of the invention must be new.

Everything that has been done in a certain field prior to the date of the device in question is technically known as "the prior art." A disclosure in the prior art is termed "a reference."

References may be classified as follows:

(a) Prior inventions, whether patented or unpatented.
(b) Prior knowledge.
(c) Prior use.
(d) Disclosures in a prior patent.
(e) Disclosures in prior printed publications.

A thing is said to be new in the eyes of the patent law, unless all its elements can be found in the same relationship in a single reference, where they are capable of doing substantially the same work in substantially the same way. If a reference effectively negatives the novelty of a device, the reference is said to be an anticipation.

A reference will not be considered a sufficient anticipation, unless it fulfills the following requirements:

(a) It must be established as having an effective date earlier than that of the invention to be anticipated.*

(b) The disclosure of the reference must be in such full and clear terms as to enable one skilled in the art to practice the invention sought to be anticipated, without the necessity of making extensive experiments.

The foregoing rules have their qualifications and limitations, which are beyond the scope of this chapter. It must, however, be strongly emphasized that a thing is not necessarily patentable just because it is new.

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* It is important to note that prior knowledge or invention, unless evidenced by patent or printed publication, must be knowledge or invention in this country.

It must also possess each one of the other prerequisites of patentability, including the all-important element of "invention."

The terms "novelty" and "invention" are not at all synonymous, although invention is often defined as "patentable novelty." It may be stated, however, that in determining novelty, the allegedly new thing is compared *qualitatively* with what went before, whereas in determining invention, a *quantitative* comparison is made.

Before leaving this subject, it is to be noted that if a device or process is old, it is wholly immaterial that the prior inventor did not know the underlying theory, or realize all the advantages of his invention. For, as we have seen, patentability cannot be predicated upon the discovery of abstract forces of nature, causes, and effects.

In the recent *Vitamin case*, 63 U.S.P.Q. 262 (C.C.A. 9, 1944), a method of irradiating food to increase its vitamin content was held invalid, because farmers had from time immemorial allowed their hay to lie in the sun to improve its food value. The fact that farmers did not know the whys and wherefores of the process was wholly immaterial.

Invention. The fourth prerequisite is that the new thing or device must have been created by the exercise of inventive ingenuity, and must involve inventions over what has gone before.

The question as to what constitutes invention is the most difficult one in the entire field of patent law. In one instance, it is possible to say without fear of contradiction that invention of a high order is present. In another case, it is possible to say that there is lacking that intangible something which distinguishes invention from mere mechanical or chemical skill. The difficulty resides in segregating and defining the intangible something so as to aid in the determination of the majority of cases, which lie in between the extremes.

In the recent *Cuno case*, 1942 C.D. 723 (S.Ct. 1941), the Supreme Court stated that to be patentable, a new thing, "however useful it may be, must reveal the flash of creative genius, not merely the skill of the calling." This statement has given rise in the Courts and to a lesser extent in the Patent Office to a much higher standard of invention. For a time it appeared that no patent, irrespective of the amount of ingenuity involved, would be held valid. Fortunately, one court after another has rejected the so-called "flash of genius" rule. As one court aptly stated (*Trabon Engineering case*, 58 U.S.P.Q. 97; C.C.A. 6, 1943):

> "Our interest is in the child; not in how or where it was born or who were its parents."

The test usually applied to determine whether a particular thing required inventive ingenuity for its creation is to ascertain whether what was produced was obvious to persons skilled in the art and acquainted with the common knowledge in that art at the date of the invention. This test involves four steps.

The first step is to ascertain in what art the invention stands, and what arts are analogous or related thereto. An inventor is conclusively presumed to know the prior art in his own and closely allied lines of endeavor, but not what has been done in remote and nonanalogous arts.

The following are a few examples of analogous arts:

(a) Preserving green corn and preserving beans, peas, fruits, etc. *Sewall v. Jones,* 91 U. S. 171 (S.Ct. 1876).

(b) Freezing ice-cream and freezing fish. *Brown v. Piper,* 91 U. S. 37 (S.Ct. 1876).

(c) Ventilating incubators and ventilating a house or room. *Jones v. Cyphers,* 126 F. 753 (C.C.A. 2, 1903).

The following are a few examples of nonanalogous arts:

(a) Method of boiling potatoes or reducing animal matter to grease and method of working asphaltum in natural state. *Pacific Contracting Co. v. Southern California Bituminous Paving Co.*, 48 F. 300 (N.D. Cal. 1891).

(b) Incubating eggs and drying tobacco. *Smith v. Snow*, 294 U. S. 1 (S.Ct. 1935).

(c) Milking cows and cleaning automobiles. *In re Luks*, 1934 C.D. 389 (C.C.P.A. 1934).

Before leaving this phase of the subject, it must be noted that reasoning by analogy in a complex field like chemistry is very much more restricted than in a relatively simpler field such as mechanics. Chemistry is essentially an experimental science, and chemical prevision is no more possible today, in spite of the great accumulation of knowledge, than it was in former times. However, in the very recent case of *Mandel Bros. Inc. v. Wallace*, 79 U.S.P.Q. 220 (S.Ct. 1948), the Supreme Court held in effect that the general store of chemical knowledge is in the public domain and that every worker in chemical fields is presumed to be thoroughly familiar therewith.

The second step is to ascertain the state of the art at a time just prior to the time that the alleged invention was made. This step is substantially the same as that involved in ascertaining whether the given device is novel.

The third step is to ascertain all the differences, both structural and functional, between the device of the alleged invention and those of the prior art. This inquiry should be pursued along lines that distinguish not merely the physical differences, but particularly the differences in functions and purposes. A conscious effort must be exerted to avoid being misled by mere superficial resemblances.

Negative Rules of Invention. The fourth step is to ascertain whether the structural or physical differences are such as would have spontaneously occurred to a person skilled in the art, if he had been faced with the problem alleged to have been solved by the new device.

In actual practice, it has been found impossible to promulgate any general rule as to what structural or physical changes in an old device or thing required the exercise of inventive ingenuity. As a result, however, of the many litigated cases there has evolved a classification of situations which recur with regularity, where the decisions are quite uniform that invention is absent. These situations are often referred to as the "negative rules of invention."

There are over twenty of such rules, but for the purposes of this discussion only a relatively few need be considered.

The first rule to be considered is that it does not involve invention to produce a device, composition, or process consisting of several component parts or elements, unless the parts or elements coact with each other in such a manner as to produce a unitary result which is not merely the aggregative effects of the individual elements.

Bond discovered that certain strains of root-nodule bacteria do not exert mutually inhibitive effect on each other, and obtained Patent No. 2,200,532 covering an inoculant for leguminous plants containing a plurality of such strains. Hence, a farmer, who had crops of clover, alfalfa, and soyabean, would not have to use three separate inoculants, but could use the same package for treating all three crops. However, the Supreme Court held the patent invalid in *Funk Bros. Seed Co. v. Kalo Inoculant Co.*, 76 U.S.P.Q. 280 (S.Ct. 1948), on the ground that the combined bacteria constituted merely an aggregation. A contrary conclusion would have been reached if the combined bacteria were shown to have properties not possessed by the bacteria individually, or produced a wholly unpredictable result.

The second rule is that it does not involve invention to replace one or more elements of an old process, device, or composition with equivalent elements.

Inventors have often contended that the rule as to equivalents should have little or no application to chemical inventions, on the ground that the action of materials in a chemical way connot be foretold, except in cases of limited and well-established, definite, and usually small groups of compounds.

In *Western Willite Co. v. Trinidad Asphalt Mfg. Co.*, 16 F. 2d. 446 (C.C.A. 8, 1926), the court agreed that the reactions and phenomena of chemistry may sometimes dictate a rule as to equivalents, which is at variance to that rule as applied to mere physical or mechanical equivalents, but stated that it would not apply a different rule to chemical inventions, except when the reactions and phenomena are latent and undeveloped.

In *National Chemical & Fertilizer Co. v. Swift & Co.*, 104 F. 87 (C.C.A. 7, 1900), a fertilizer made by adding iron *sulfate* to waste liquors from slaughter houses containing gelatinous matter and albuminoids was held unpatentable, because a similar material had been made by a similar process wherein *aluminum salts* had been added to the waste liquors.

A corollary of the rule as to equivalents is that it does not involve invention to utilize a homologue or isomer of an old compound.

Homologues and isomers are substances of substantially similar chemical constitution. Hence, a new compound, which is a homologue or an isomer of an old compound, is not patentable, unless it has unobvious or unexpected beneficial properties not possessed by the known compound.

For this reason, 2-nitro-2-pentene was held unpatentable over 2-nitro-2-butene (*in re Hass*, 60 U.S.P.Q. 544 (C.C.P.A. 1944)). Likewise, 1-chloro-2-amino-pentene was held unpatentable over a lower homologue, and also unpatentable over the N-diethyl isomer (*in re Lincoln*, 53 U.S.P.Q. 40 (C.C.P.A. 1942)).

The term "homologues" is restricted to compounds differing by CH_2 or a multiple thereof. Hence, in a recent case, naphthyl methyl compounds* were held patentable over the corresponding benzyl (phenyl methyl) compounds (*in re Jones*, 65 U.S.P.Q. 480 (C.C.P.A. 1945)).

Newly produced homologues or isomers of well-known compounds may be patentable, if they have unexpected or unpredictable uses.

If ethyl alcohol (ethanol) were a newly invented compound, it would be patentable over methyl alcohol (methanol). For despite the fact that ethyl alcohol is usually listed as a homologue of methyl alcohol, these substances differ considerably in their properties. Many persons to their consternation ascertained this fact with blinding results during the prohibition era.

Di-(beta-chlorethyl) sulfide is the deadly mustard gas used in chemical warfare, whereas the corresponding alpha-chlor derivative is practically innocuous. Hence, these compounds, although position isomers, are patentably different.

Certain mono- and dihalogen substituted 8-hydroxyquinolines were held patentable, because they were excellent insecticides whereas their isomers are practically inert (*in re Senn*, 71 U.S.P.Q. 273 (B.A. 1946)).

The third rule is that it generally does not constitute invention to utilize an element or expedient which is old in the same or in an analogous art or which is common to several diverse arts.

It is old to use organic solvents as carriers for agricultural chemicals such as insecticides, plant stimulants, weed killers, etc. Hence, in *In re*

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* These compounds are very superior insecticides.

Migrdichian, 108 F. 2d. 237 (C.C.P.A. 1939), it was held unpatentable to make a fumigant by dissolving cyanhydrin, which is a well-known fumigant, in an organic solvent, and in *Ex parte Billman*, 71 U.S.P.Q. 253 (B.A. 1946), a patent was refused for a solution of a composition intended for use as a plant stimulant.

In *Scientific Tablet Co. v. Ossege*, 125 F. 2d. 151 (C.C.A. 6, 1942), it was held not to constitute patentable invention to add salt in the form of tablets instead of in bulk to tomatoes as they were being canned.

The fourth rule is that it does not constitute invention to apply an old series of steps or operations to a material having a composition or properties similar to those of a material previously used in the process.

A corollary of this rule is that it does not involve invention to utilize an old type chemical recation to make a specific compound, even though said compound had never been made that way.

This rule, which was laid down in *In re Wietzel*, 5 U.S.P.Q. 177 (C.C.P.A. 1930), is often stated as follows: If the prior art teaches a process for making one chemical compound and there is reason to suppose that the process could be used to make another compound of related structure, it would not involve invention to try out the process to find that it can be used for making the latter compound.

The fifth rule is that it does not involve invention to select judiciously from a list of previously used substances those that give desired results.

It was old to make paints by incorporating insecticides in a coating composition. Hence, it was held not to constitute patentable invention to combine DDT with a particular coating composition, although the product had greater insecticidal persistency than prior paints. The greater persistency was a known and inherent property of DDT, and was not enhanced by the combination (*ex parte McClane*, 78 U.S.P.Q. 216 (B.A. 1948)).

The literature of insecticides lists pyrethrins, rotenone, sodium fluoride, and kerosene as contact and stomach poisons for roaches. An insecticide for roaches consisting of sodium fluoride, pyrethrins and kerosene was refused patent protection (*in re Campbell*, 171 F. 2d. 321 (C.C.P.A. 1948)).

The sixth rule is that it does not involve invention to change the physical condition or degree of purity of a well-known chemical composition unless the change produces an unobvious or disproportionate result.

In *Milligan & Higgins Glue Co. v. Upton*, 97 U. S. 3 (S.Ct. 1878), a solid glue in comminuted state was held unpatentable over ordinary glue, though it was more readily soluble and could be more conveniently packed.

The "Aspirin" patent (acetylsalicylic acid) was sustained on the ground that by reducing the amount of impurities, Hoffman, the patentee, had converted a deleterious substance long known to chemists into a valuable medicine. *Kuehmsted case,* 179 F. 701 (C.C.A. 7, 1910).

Calcium carbide in the form of aggregated crystals was held patentable over the amorphous compound, which was worthless commercially, unfit for use in gas generators and rapidly deteriorated when exposed to the air. *Union Carbide case,* 181 F. 104 (C.C.A. 2, 1910).

The seventh rule is that it does not involve invention to change the proportions of the ingredients of a well-known composition.

It was shown to be old to dissolve celluloid in camphor and alcohol. Patent No. 97,454, which was based on the idea of using less alcohol than previously, but still of sufficient strength for the purpose, was invalidated in *Spill v. Celluloid Mfg. Co.,* 21 F. 631 (S.D.N.Y. 1884).

A British patent to Geigy disclosed a spraying composition containing DDT and casein. In *Ex parte McClane,* 78 U.S.P.Q. 216 (B.A. 1948), it was held not to be patentable to change the proportions of DDT and casein to produce a coating composition.

A situation not covered by the rules above considered occurs in *In re Campbell,* 171 F. 2d. 321 (C.C.P.A. 1948). A method of applying an insecticide for roaches containing sodium fluoride so that it would adhere consisted in spraying the material through "a pin stream under low pressure." The Court in refusing patent protection stated:

> "We find no reason why one skilled in the art would not realize the kind of stream and the proper pressure to employ in spraying an insecticide. . . ."

Disproportionate Result. It should be emphasized that no matter how simple or obvious an invention may appear after it has been made, it is nevertheless patentable if it has produced a disproportionate or unobvious change in result or solved a difficult or previously unsolved problem.

It was held patentable in an old case to add a small piece of aluminum to molten iron just as it was to be poured into the mold, because this relatively simple expedient successfully solved the problem of making a casting free of blow holes. *United States Mitis Co. v. Midvale Steel Co.,* 135 F. 103 (E.D. Pa. 1904).

A sealing composition for tin cans consisting simply of latex and bentonite was held patentable in a recent case. *Dewey & Almy Case,* 52 U.S.P.Q. 138 (C.C.A. 2, 1942).

In the *Edwards case,* 52 U.S.P.Q. 91 (C.C.P.A. 1941), it appeared that Edwards had by the exercise of inventive genius discovered the reason why cement slurries for sealing oil wells failed to set properly. An obvious solution of the problem was accorded patent protection.

In *Ex parte Nees,* 66 U.S.P.Q. 271 (1944), a reversal of steps in a process of making sodium perborate was held patentable because the change in process resulted in a product of low bulk density.

Forfeiture of Right to Patent Protection. The fifth requirement for the grant of a valid patent is that the inventor must not have abandoned his invention or otherwise forfeited his right to patent protection.

The following are some of the ways in which an inventor may lose his right to patent protection:

(a) By indicating either by express words or by his conduct that he does not intend to obtain patent protection or to preclude the public from availing itself freely of the invention.

(b) By suppressing and concealing the invention until he is spurred into renewed activity by knowledge that a rival inventor has entered the field.

(c) By allowing one year to elapse after a public use or offer for sale of the invention has occurred before filing a patent application.

(d) By practicing the invention as a trade-secret without filing a patent application.

(e) By allowing a year to elapse after the device has been described in a patent or printed publication before filing an application.

(f) By securing a patent in a foreign country without having filed an application for the same invention in this country within six months in the case of a design invention, and within twelve months in the case of the other classes of invention.

(g) By violation of a war order enjoining secrecy issued by the Commissioner of Patents.

(h) By failure to take the proper steps to set aside a final rejection of an application by the Patent Office.

Rule Against Double Patenting. The sixth prerequisite to support the grant of a valid patent is that its subject matter must be patentably distinct from that of any prior patent issued to the same inventor.

An inventor cannot obtain two valid patents on the same invention, whether or not they are couched in the same language and whether or not they are issued on the same day.

An inventor cannot obtain separate patents on different species or embodiments of the same broad or generic invention unless the different species are patentable over each other.

An inventor cannot obtain broad protection on an invention for which he has already obtained specific protection. The two applications must disclose two different embodiments of the generic invention, and the broad invention should be covered by the application first to be issued.

An inventor cannot ordinarily obtain a patent on an improvement on his prior patent, unless the improvement involves invention over the prior device.

Patent Applications. The seventh requirement for patentability is that the inventor must file an application in the United States Patent Office adequately describing and clearly defining the subject matter of the invention and prosecute it to allowance.

The application must be made by the inventor only. If more than one person contribute mutual suggestions which result in a unitary invention they are joint inventors and all must join in making the application. If any of them neglect to join, the patent will be held invalid; similarly if a person who had no part in making the invention files the application or joins with the true inventor in filing the papers. In this connection it must be emphasized that one who makes a financial contribution and nothing more is not a joint inventor. The only way he can acquire an interest in the patent is by assignment from the true inventor.

The mere fact that one who conceives an invention avails himself of the constructive skill and ingenuity of another to reduce the inventive idea to practice does not make the second person a joint inventor. And this is so, even if the second person makes valuable discoveries ancillary to the plan and preconceived design of his employer. But if the second person makes suggestions which modify and make the main idea operative or contributes an independent part of the entire invention which combines with the part produced by the other to create the whole, he is entitled to be considered a joint inventor and must join in filing the application. Furthermore, if the second person is merely given a problem in very general terms or finds it necessary to discard or depart radically from the plans of his employer, he is a sole inventor and the application must be filed by him alone. Under proper circumstances, however, the patent, when issued, may belong to the employer or he may be given a shop right therein.

The Specification. The part of the application describing the invention is called the specification and must be in such full, clear, concise, and exact terms as to enable any person skilled in the art or science to which the invention or discovery appertains to make, construct, compound, and use the same. The withholding of any information essential to the working of the invention is sufficient to invalidate the patent. In the case of devices that can be illustrated, the specification must be supplemented by a drawing.

Since the description is directed to those skilled in the art, it is unnecessary for the applicant to point out the relationship between his particular improvement and the prior art devices. In the language of the Supreme Court, the patentee need only "begin at the point where his invention begins, and describe what he has made that is new and what it replaces of the old. That which is common and well known is as if it were written out in the patent and delineated in the drawings."

Neither is the inventor required to state all the advantages and functions of his invention or all the uses to which it may be put. Likewise, he may omit from his application the scientific principles or theory underlying his invention or the causes which produce the desirable result. And if he does state what he believes to be the principles governing his discovery, it is wholly immaterial to the validity of the patent whether or not the statement is correct, so long as he has so set forth the thing to be done that it can be reproduced by one skilled in the art.

The Claims. At the end of the specification are one or more short statements called "claims." The claims are the vital part of the patent and define the scope of the patent. Great skill is required in drafting them. Usually the patent examiner does not agree with the inventor that the presented claims represent his contribution to the art. In such cases the inventor may amend the rejected claims or try to persuade the examiner to his own way of thinking. When the inventor and the examiner finally agree, the patent is granted with the claims agreed upon. If they cannot agree, the inventor may appeal to a higher tribunal in the Patent Office and then to the courts. But if the inventor acquiesces in the rejection of a claim and the patent is granted with a narrower claim, he is forever estopped from contending that he was entitled to the broader claim.

Each claim in a patent is considered a separate and independent invention. One may be valid, all the rest invalid. But the claim that is good remains good and is unaffected by the presence of those that are bad. Likewise, one claim may be infringed and the others not. In other words, the patent does not stand or fall as a unity—each claim is in effect a separate patent. However, if some of the claims of a patent are finally held invalid, the patentee must within a reasonable time file a disclaimer in the Patent Office as to the claim held invalid. Otherwise he will not be allowed to bring an infringement suit on the claims held valid.

RIGHTS CONFERRED BY PATENT

In conclusion, it must be noted that a patent does not confer upon the inventor the right to use his own invention. He would have this right in the absence of the patent laws. All the patent gives the inventor is the right to exclude others from using the invention.

It follows from what has been said that there are situations in which the patentee may be restricted in the use of his invention or even entirely precluded. Thus it has been decided that inventors of butter substitutes, patent medicines, adulterated foods, and gambling devices cannot vend these articles in states prohibiting their sale. By the same token, owners of patents covering insecticides, weed killers, and other agricultural chemicals must comply with national and local regulations as to their sale and manner of use.

It also follows that an inventor of an improvement on a prior dominating patent cannot use the improvement until the dominating patent expires. He can, however, prevent the owner of the dominating patent from using the improvement. In this way, he may induce the prior patentee to exchange licenses with him and thus put both patents to work over a much larger field.

It is important to note that the patentee need not use his invention or permit others to do so. The only hope that the public has that an inventor will make his invention immediately available to them is the expectation that his self interest will induce him to do so.

The patentee may sell or assign his invention or grant licenses under his invention. The consideration for the assignment or license may be a lump sum or royalties paid over the life of the patent. The assignment or license may carry various conditions with it, but the patentee may not use the patent as a cloak to violate the antitrust laws. It follows that the patentee may not utilize the patent to control or suppress competition in unpatented materials. Hence, the owner of a patent on a chemical weed killer cannot compel licensees to buy the unpatented ingredients from him or to purchase unpatented spraying equipment from him.

Chapter XXIV

CHEMURGIC APPLICATIONS OF AGRICULTURAL PRODUCTS

John R. Clopton

University of Colorado, Boulder, Colo.

For centuries agriculture has supplied raw materials for industry on a limited scale, only a few industries such as those manufacturing processed foods, textiles, paper, leather and paint being entirely dependent on agriculture for their raw materials. Agriculture has had for its main objective the provision of the three essentials of life—food, clothing, and shelter.

However, in recent years, a gradually increasing interest has developed in agriculture as a producer of industrial raw materials. This interest has been intensified by periods of farm surpluses as well as by periods of war and postwar scarcities, during which agriculture is forced to meet the needs of industrial emergencies. Interest is stimulated even further by knowledge of the fact that many nonrenewable natural resources such as petroleum, coal, iron ore and other minerals are being depleted at ever-increasing rates. As a matter of necessity, industry must turn, whenever possible, to the utilization of materials that can be produced as rapidly as they are consumed. Farm produce is renewable with each growing season, and oftentimes more than one crop per year can be produced.

Events during the past twenty years, including a severe economic depression and burdensome agricultural surpluses followed by the most destructive world conflict in history, have emphasized chemurgic developments to a point where organized action is being taken to increase the industrial utilization of plant materials. The four Regional Research Laboratories, and various other laboratories of the United States Department of Agriculture were established for this purpose. Throughout the country there are many other research organizations, some affiliated with educational institutions, some sponsored by industry, and some maintained by private gifts and endowments, all working directly or indirectly toward this same objective. The trend is consistently toward the more efficient and complete utilization of plant materials to satisfy man's needs.

The industrialist is very seldom concerned with the nature of the sources of his raw materials so long as they meet his needs with regard to quantity, price, and quality. He, therefore, looks to agriculture, not as a grower of wheat, corn, rice, soybeans, etc., but as a producer of raw materials from which such things as starch and dextrins, paints and varnishes, fabrics, building materials, plastics, cosmetics, and medicinals may be manufactured.

TABLE 122. SOURCES AND INDUSTRIAL USES OF AGRICULTURAL MATERIALS

Materials	Principal Sources	Principal Uses
Essential Oils	Citrus fruits, peppermint, spearmint, lemon grass, Dalmatian sage, lavendar, goldenrod, French marjorum, rose, jasmine, anise, bergamot, coriander, thyme, vanilla, cedar, pine, birch, cherry laurel, horsemint, and many others.	Perfumes, cosmetics, chewing gum, incense, condiments, soaps, dentifrices, medicinals, insecticides, pastries, candies, beverages, soaps.
Tannins	Quebracho extract, chestnut extract, Tara powder, wattle extract, myrobalans, divi divi, sumac leaves, hemlock, oak and mangrove bark.	Tanning agent for leather and hides, dyeing, glues, adhesives, metallurgy, paper, photography, beverages, inks, cosmetics, pharmaceuticals, and chemical reagents.
Alkaloids	The six plant families: Leguminosae, Apocynaceae, Papaveraceae [poppy], Solanaceae [nightshade], Rubiaceae [madder] and Ranunculaceae [crowfoot]. Also some in Labiatae, Rosaceae and Compositae families.	Medical practice including numerous specific uses, insecticides, beverages [cocoa, coffee, tea], special chemical reagents.
Enzymes	Various plant tissues and cell sap, animal gland extracts, yeast, molds and fungi.	Digestive aids, prepared foods, tenderizing meats, dehairing hides, cheese manufacture, clarification of beverages and fruit juices, degumming textile fibers, fermentation processes, baking.
Rubbers	Latex of many species of tropical trees [especially *Hevea brasiliensis*], guayule, and cryptostegia.	Tires and inner tubes, rubberized fabrics, electrical insulation, construction materials for automobiles, airplanes, home appliances, hospital and laboratory supplies, shoes, containers, linings, cements, adhesives, plastics, shock absorbers, chewing gum.
Pigments [chlorophyll, carotenoids, etc.]	Pigmented plant tissues such as alfalfa [chlorophyll] and carrots, logwood, cuba wood [fustic], and osage orange [osage crystals], egg yolks.	Coloring for foods, perfumes, candles, petroleum products, resins, waxes, olive oil, soaps, and as deodorant; textile dyes, wood dyes for toys.
Gums and Resins	Various species of trees yielding exudates which solidify in air: acaroides, mastics, sandaracs, copals, dammars, elemis, dragons blood, guaiacum, balsams, ammoniacum, myrrh, galbanum, asafoetida, gambage, sagapenum, frankincense, scammony, jalap, podophyllum, gutta-percha, chicle, jelutong, balata.	Varnishes, paints, lacquers, glues, adhesives, inks, paper, oilcloth, linoleum, textiles, chewing gums, soaps, insecticides, plastics, synthetic resins, cosmetics, pharmaceuticals, electrical insulation, polishes, photographic chemicals, waterproofing.
Vitamins and Hormones	Citrus fruits, green vegetables, carrots, yeast, eggs, seeds, animal glands and organs.	Pharmaceuticals, enriched foods, cosmetics.

TABLE 122—CONTINUED

Materials	Principal Sources	Principal Uses
Starches	Corn, tapioca, white, potatoes, wheat, sweet potatoes, arrowroot, sago, waxy sorghum, waxy maize, rice.	Adhesives, textile and paper sizing, laundry, potash and aluminum refining, dry cell batteries, dusting compound for rubber goods and gums, drilling mud stabilizer, explosives, drugs, cosmetics, alcohol and other chemicals, syrups, dextrins, sugars, other foods.
Sugars	Sugar cane, sugar beet, sugar maple, grapes, various fruits, agricultural wastes [by saccharification].	Fermentation [to alcohol and other chemicals], cosmetics, pharmaceuticals, pastries, candies, syrups, and prepared foods.
Fats and Oils	Soybeans, cottonseeds, peanuts, corn germs, flax seeds, coconuts, castor beans, palms, olives, sunflower seeds, safflower seeds, sesame seeds, tung seeds, oiticica seeds, perilla seeds, animal fats [butter, lard, tallow, fish oils].	Shortening, salad oils, cooking oils, margarine, cutting oils, lubricants, paints, varnishes, plastics, medicines, cosmetics, polishing compounds, emulsions, rubber substitutes and rubber extenders, soaps, glycerine manufacture, fatty acid manufacture.
Waxes	Palm leaves, [Carnauba and Ouricury], Japanese Sumac [Japan], Candelilla, Ucuhuba, reeds, flax, cane, cotton, insects [bees], whales [spermaceti].	Polishes, paints, varnishes, plastics, dental work, candles, crayons, stencils, adhesives, paper coatings, inks, insulation, preservatives, pyrotechnics, cosmetics, pharmaceuticals, leather finishes.
Fibers	Cotton, flax, jute, ramie, sisal hemp, broom, wool, silk, hair, feathers, kapok, casein, vegetable proteins.	Textiles, rope, netting, twine, burlap, paper, insulation, shock absorbers, mats, rugs, carpets.
Pectins	Apple pomace, citrus fruits.	Gels, emulsions, jams, jellies, prepared jellos, home canning, pharmaceuticals and cosmetics.

The principal materials obtainable directly from plant sources include the following:

- Starches
- Sugars
- Cellulose
- Fats and Oils
- Waxes
- Proteins
- Fibers
- Pectins
- Enzymes
- Pigments
- Rubber
- Gums and Resins
- Alkaloids
- Tannins
- Essential Oils
- Vitamins

Many large industries are devoted to the processing of plant materials for one or more of the above-mentioned products. These in turn provide raw materials for a great many other industries wherein they are modified physically and chemically or combined with other materials to produce innumerable forms of finished products. A brief summary of some of the more important products and their industrial applications is presented in Table 122.

Only a condensed survey of this rapidly growing field, which is uniting industry and agriculture, can possibly be presented in a single chapter. However, it is hoped that the reader may find the presentation complete enough to emphasize the full scope of the subject and its trends, and that by its perusal he may be stimulated to further study and appreciation of its importance.

For the sake of simplicity the subject matter is organized under the following headings:

Cereal Grains
Fruits and Vegetables
Nuts and Oil Seeds
Forage and Fiber Crops
Forest Plants
Specialty Crops
Agricultural By-Products and Wastes
Animal Products

CEREAL GRAINS

The cereal grains constitute the largest and most important group of agricultural commodities, with rice, corn, and wheat standing as the three most important food sources of the world. From an industrial standpoint the cereal grains are considered principally as sources of carbohydrate and protein materials. They are rich in starch and compete with roots and tubers as sources of this very valuable raw material.

In the United States corn is the top ranking cereal crop with an annual production of about 3 billion bushels. About 90 per cent is used directly for feeding purposes on the farms; the remaining 10 per cent is used in industry and for the most part is used in the preparation of corn cereals, cornmeal, hominy, and mixed feeds. About 3 per cent of the total is used in the manufacture of cornstarch. Nevertheless, this amounts to a yearly production of over 1 billion pounds and makes corn by far the leading source of starch and greater than all the other sources combined.

About 500 million pounds of starch, four-fifths of which was tapioca starch, have been imported each year in the past. Tapioca starch is highly valued in industry and is superior for many purposes because of the clarity of its gels and its viscosity characteristics. These properties are attributed to the presence of 95 to 98 per cent of amylopectin (the branched chain starch) in its starch composition. Ordinary cornstarch contains no amylopectin but is made up entirely of the unbranched starch molecules called amylose. However, through methods of plant breeding a variety of "waxy" maize and "waxy" sorghum has been developed which yields starches containing amounts of amylopectin comparable with that of tapioca starch and these starches are replacing tapioca starch. A new starch plant at Corpus Christi, Texas, is processing "waxy" sorghum exclusively.

In addition to its value as a source of starch, corn is processed for other useful materials. Corn germ oil is well known as a high quality edible oil and is widely used in the manufacture of salad oils, cooking oils, margarine, and shortening. The corn embryo (germ) is separated from the seed during the milling operations and the oil is obtained by pressing or by extraction with a suitable oil solvent. During wet milling operations corn is steeped for a period of time in large vats. The steep liquor is now used, in part, to promote the production of penicillin. Yields of penicillin have been increased several hundredfold by the use of corn steep liquor in *Penicillium* cultures. Large quantities of corn are consumed by the fermentation industries which, contrary to popular viewpoints, are not confined to the production of ethyl alcohol alone. A number of other chemicals such as butyl alcohol, butylene glycol, glycerol, acetone, citric acid, lactic acid, gluconic acid, and acetic acid are produced by the action of yeast and other microorganisms on carbohydrate substrates. Over 10 million tons of grain and molasses are used each year by the fermentation industries. Corn mash water is a valuable source of gluten. A protein-prolamine (zein) extracted from corn has proved useful in the production of synthetic fibers, resins, protective coatings, inks and plastics. By hydrolysis cornstarch yields glucose which can be reduced electrolytically to sorbitol or mannitol. Sorbitol is a valuable flexibilizer and humectant. Over 200 industrial products are derived from corn as a raw material.

With the exception of barley, the other cereal grains are not industrialized appreciably beyond their utilization in various foods and feeds. Wheat is not processed extensively as a source of starch because of the difficulty in separating the starch from the sticky dough-like gluten which forms during the washing operations. Other cereal starches of minor importance are obtained from rice and barley. Tuber and root starches will be mentioned later. Barley is the most highly industrialized grain considering the percentage utilized by industry. Approximately 25 per cent of the barley crop is used in the malting and brewing industries and in the preparation of malt syrups, malted flour, and malted milk. The annual yield of barley is about 250 million bushels.

FRUITS AND VEGETABLES

Fruits are marketed almost entirely for direct consumption as food. As in most other cases where farm products are marketed as food, quality standards require the culling out of off-grade materials, and this is particularly true of fruits. In some cases processes have been developed for the utilization of off-grade fruits. For example, poor and damaged apples are processed for cider and vinegar and the remaining pomace or pulp is a principal source of pectin. Also apple pomace is the main source of ingredients for apple syrup (apple nectar) which is used, among other things, as a humectant and tobacco flavor. Approximately 25 million bushels of cull apples are produced annually.

Oranges and lemons yield essential oils which are used as flavorings and perfume constituents. Grapefruit seeds are processed on a small scale for fixed oils.

Grape seed oil is a useful drying oil and grape skins and stems yield tannic acid and charcoal for use in gas masks and decolorization processes. Wine lees (argols) yield citrate and malate salts as well as tartrates. They are useful as photographic chemicals, medicinals, and baking powder ingredients.

Cranberry pulp has been found to be a very rich source of ursolic acid (10 per cent of the skins or about 6 per cent of the weight of the dried pulp). This acid is able to produce water-in-oil emulsions at concentrations of 3:1000 of ursolic acid. Cranberry seed oil and cranberry wax are also recovered.

Cull avocados or those not reaching calavo specifications are processed for the oil they contain. All the present production of avocado oil is consumed in the cosmetic trade.

While the papaya fruit is very appealing as a food, it serves also as a source of the proteolytic enzyme papain which is used so widely in medicine and prepared foods. Bromelin, an enzyme obtained from pineapple, is almost identical in its action to that of papain and is used for the same purposes.

Vegetables, like the cereal grains, store up carbohydrate materials, and in some cases they provide economical sources of these materials to industry. Various root and tuber plants such as white potatoes, sweet potatoes, maranta roots (arrowroot) and manihot (tapioca or cassava) are veritable storehouses for starch. About 25 million pounds of potato starch are produced annually in the United States. Usually the poorer grades or cull potatoes are used for starch production. In recent years several plants have been processing sweet potatoes for starch. This starch is of good quality and suitable for many industrial uses.

The sugar beet is a well-known source of sucrose and competes with sugar cane as a major source of this sugar. As a by-product of the sugar beets processing plants, sugar beet pulp is used mainly as a stock feed. However, quantities are now used in the production of yeast and citric acid.

The large scale processing of vegetables and fruits by industry is handicapped by their perishability. It will be seen how this factor is reckoned with by observing the location of industries using such materials. The processing plants are strategically located in the producing areas and are operated on a seasonal schedule following each harvest. In some cases, such as in handling sweet potatoes, the crop may be dehydrated and stored so that processing plants may be operated over a much longer period, if not the year around.

Nuts and Oil Seeds

Those crops which are harvested and processed for the fats they contain are referred to as oil-seed crops. The oil content varies from a few per cent in some cases, up to 60 or 70 per cent in others. The annual production of fats in the United States is around 10 billion pounds of which about 40 per cent is of animal origin (butter, lard, tallow, etc.) and the rest of vegetable origin. The outstanding source of vegetable fat has been cottonseeds with a yield of over 1 billion pounds a year. However, there has been a gradual decline in cotton production and at the same time a phenomenal increase in soybean production, with the result that in 1945 cottonseed oil surrendered its place at the top of the list to soybean oil. Approximately 70 per cent of all fats are used as foods, 20 per cent for soaps, 6 per cent for drying oils and 4 per cent for miscellaneous purposes.

Most satisfactory edible fats are obtained from such sources as the coconut, palm, palm kernel, olive, peanut, cottonseed, corn germ, sunflower seed, and sesame seed. Intensive research has resulted in the improvement of the flavor characteristics of soybean so that it can be used rather freely in admixture with edible oils. The best drying oils useful in the protective coating industries are linseed, tung, perilla, oiticica, and safflower oil. In addition, soybean and castor bean oils can be converted into good drying oils by simple chemical treatments. Oils such as rapeseed and mustard seed oils are useful in industry for the preparation of lubricants, factices, and numerous other purposes but are not well suited for use as drying oils or in foods.

In the manufacture of edible products such as shortening and margarine there has been a definite trend from animal to vegetable fats. Whereas these products were formerly produced largely from animal fats, over 90 per cent of the fats now used for this purpose are of vegetable origin.

The nonfood uses of fat products in industry are gradually expanding. It should be remembered that fats serve as raw materials from which the various fatty acids and glycerin are obtained. The industrial importance of glycerin cannot be overemphasized, and its uses are too numerous to mention here. Fatty acids are used in large volumes for the synthesis of drying compositions, the formation of polymers for use in coatings and rubber substitutes, and in the production of dibasic acids now used in the manufacture of nylons.

Several of the vegetable fats have special and specific medicinal values. Castor oil is well known as a cathartic, and chaulmoogra oil has been used for centuries to treat leprosy. Of the fatty acids, linoleic acid is a dietary essential and is classified among the vitamins. Various metal salts of the fatty acids, such as zinc stearate, are used extensively in medicaments, dusting powders, polishes, etc. Undecylenic acid and its zinc salt are very effective in the treatment of fungous infections like scalp ringworm and athlete's foot.

Lauric and palmitic acids find special applications in the synthesis of soapless detergents.

After the oil is removed from oil-rich seeds or nuts, the residual meal is usually rich in protein. It is often referred to as oil-cake or oil-seed meal. Generally this material is blended with various feedstuffs which are for the most part too rich in carbohydrate constituents for optimum feeding quality. In some instances the proteins are extracted from the meal and used in the manufacture of synthetic fibers, glues, adhesives, plastics, etc. That is being done with soybean meal.

The general scarcity of protein materials coupled with the technical difficulty of obtaining them economically in pure form from their natural sources may help to explain the reason why proteins are utilized to such a limited extent industrially as compared to the carbohydrates and fats. It is true, of course, that plants do not store up reserve supplies of proteins as they do of carbohydrates and fats.

Forage and Fiber Crops

From an industrial standpoint very little direct use is made of forage crops. It may be sufficient to mention the small-scale use of alfalfa as a source of vitamin A and chlorophyll and that a number of alfalfa dehydration units are operating in the midwest and southwest.

Fiber crops are the true industrial crops and are utilized by the nonfood industries in the manufacture of many types of textiles, ropes, twines, mats, insulation, etc. The fiber plants have provided man his clothing materials and much of his shelter.

There are over one thousand species of fiber plants known, although fibers of commercial importance are relatively few in number. Fibers of commercial importance are furnished by several different plant families, most of which occur in the tropics. However, cotton, flax, hemp, ramie, and jute are suited to subtropical and temperate regions.

Cotton is considered the greatest industrial crop in the world, and the chief fiber plant. About 26 million bales are produced each year of which about 40 per cent is produced in the United States. In addition to its use as a textile fiber, cotton is the purest natural source of cellulose and for this reason considerable amounts of it are used in the preparation of cellulose derivatives, which are made into explosives, lacquers, and various plastics.

At one time the cotton seed with its fuzzy covering of linters was discarded as worthless waste. Cotton seeds are now a valuable source of oil, the meal is utilized as a protein-rich feed, and the linters furnish waddings and stuffings and low-grade fiber. The hulls are also being used as a source of furfural, in fertilizers, etc.

Flax is second only to cotton in importance as a fiber. From its fibers linen fabrics and finest quality writing paper are made. It has been known and used since prehistoric times. Its great tensile strength and durability makes it useful in threads, twine and high quality fish and seine lines. At present very little fiber flax is grown in the United States, most of it being produced in the Northern European countries.

In regions of low rainfall flax is grown for its seed which is the source of linseed oil.

Of the minor fiber crops, hemp, jute, ramie and sisal are worthy of mention. Hemp fibers are noted for their length (3 to 9 feet), strength, and durability and are used for rope, twine, burlap, carpets, sailcloth, valve packings, and paper. Jute is used for somewhat the same purposes as hemp. Ramie is the strongest fiber known but it is not generally used in this country because the treatment necessary to remove the fibers is so expensive. Large amounts of sisal are used in the production of binder twine. Most of the supply comes from Mexico and the Dutch East Indies. Brushes are made from piassava, palmyra, kittul, broomcorn, and broomroot. Hat fibers come from wheat, rice, barley, rye straw; Panama hats are made from selected young leaves of *Carludovica palmata,* a stemless palm cultivated in Colombia and Ecuador. Puerto Rican hats are made from the leaves of the hat palm, *Sabal causiarum.*

Kapok, milkweed, and cattail fibers are very light weight and impervious to water. For this reason they are used as filling for life preservers and cushions and as insulation.

The industrial importance of the animal fibers, wool, silk, and mohair, is well known and a discussion of them here will be omitted. Attention is called to the various synthetic fibers such as nylon, rayon, celanese, glass, casein, and the various plastic sheet materials that are entering the field in competition with natural fibers and paper. Such synthetic products focus attention on the fact that science is ever trying to improve on nature and that many a long standing industry shall pass into oblivion to be replaced by those making new and superior products.

Forest Plants (Trees)

A full description of the various industrial applications of forest products would easily require an entire volume. Wood is by no means the only useful material obtained from trees, and the woods themselves are now modified physically and chemically in numerous ways to suit our needs. The natural characteristics of wood no longer decide the limitations of its uses. Soft woods such as poplar can be made as hard as maple by impregnation with methylol urea before the kiln drying process. A resin is formed in the wood during the heating and imparts the added strength and hardness. Wood treated in this manner is dimensionally stable and has greater tensile strength, which is the same in all directions. It takes a high polish and has increased wearing qualities. When wood is impregnated with urea and then heated, it becomes pliable and may be set to any desired shape, which is retained on cooling.

Wood is made fire resistant by treatment with $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, $MgHPO_4$ and H_3PO_4.

Tremendous quantities of wood are used in the manufacture of paper, such quantities that wood for this purpose is becoming increasingly difficult to obtain, particularly for making newsprint. In this connection an extremely valuable contribution has been made by the Herty Laboratory of Savannah, Georgia, in bringing about the successful production of newsprint from the Southern yellow pine. This process has created an expansion of the southern paper industry amounting to over 200 million dollars.

It is encouraging to observe the development of processes designed for the more efficient and complete utilization of forest products for in the past our forest resources have been wasted to a shameful degree. In this connection new industries are utilizing sawdust and mill wastes in the manufacture of sugar and alcohol. (One ton of sawdust will yield 1000 pounds of plastic ingredients, 120 pounds of methyl alcohol, 500 pounds of sugar, about 60 pounds of furfural, and smaller amounts of other valuable products.) Wood flour of various grades, useful in the plastics, linoleum, and other industries, is made from wood waste. About 65,000 tons of wood flour are produced annually in the United States. The distillation of wood yields over 100 valuable chemical compounds, including methyl alcohol, turpentine, acetic acid, ammonia, acetone, pine oils, and pyroligneous acid.

Large areas of pine stumps are now being uprooted and processed for turpentine, rosin, and pine oil. Approximately 8 gallons of turpentine, 4 gallons of pine oil, and 300 pounds of rosin are obtained from one ton of long leaf pine stump wood. About 40 million dollars worth of these materials are produced annually in the South.

SPECIALTY CROPS

There are a number of crops of considerable commercial importance that are cultivated for more or less special purposes. One major crop of this type is tobacco. In addition to being an exclusive smoking material, it is the source of the alkaloid, nicotine, which is used extensively as an insecticide and a starting material in the synthesis of niacin (nicotinic acid). Recently it has been found that buckwheat, tobacco and the northern chokecherry are relatively rich sources of rutin, a compound used in treating diseases involving capillary fragility.

Other specialty crops include pyrethrum, which is a valuable source of the insecticides, pyrethrins and cinerins (see Chapter XX), the drug-producing plants, and those yielding essential oils. During the war three-fourths of our imports of essential oils were cut off, but it was soon found that the deficiency could be made up by oils produced in various sections of the United States. Peppermint, spearmint, and wormwood oils are produced in Michigan and Indiana. Wintergreen, cedarleaf oil, and other wood aromatics are produced from northeastern woods. Wormseed oil comes almost exclusively from Maryland. Other essential oils produced in the United States include lemongrass oil, erigeron oil, oil of tansy, dill, pennyroyal, Dalmatian sage, French marjoram, Spanish thyme, Italian lavender, camphor, rose, goldenrod, etc.

Some of the new industrial crops are gaining steadily in importance. Guayule and cryptostegia are potential new sources of rubber. Guar, *Cyamopsis proraloides* or *C. tetragonloba*, a plant introduced from India, is attaining marked recognition as a rich source of mannogalactan mucilage. This gum is a superior paper coating material which imparts greater tensile strength and surface qualities.

AGRICULTURAL BY-PRODUCTS AND WASTES

By far the greatest quantities of agricultural by-products and wastes occur on the farms in the form of bulky and fibrous materials such as cereal grain straw, corn stalks and cobs, vines, sugar beet tops, seed hulls, etc. The volume of unused farm wastes probably exceeds 200 million tons annually. Only a very small percentage of these materials are now used by industry. They are used in making building materials such as fiber boards and Masonite and to a limited extent in paper making. Sugar cane bagasse is finding similar use in the manufacture of Celotex. Corn cobs are ground, screened, and used as an abrasive to clean and burnish metal surfaces and tinplate after the plating process. They are also used for cleaning furs. Next to oat hulls, corn cobs are the most valuable source of furfural which is assumming tremendous importance as an industrial chemical.

There are numerous agricultural residues and by-products that space does not permit mentioning in detail. Generally speaking their utilization is handicapped by their widely scattered distribution and the high cost of transporting materials of such bulkiness. Economic considerations usually make it impractical to transport such materials beyond about a hundred miles of the processing plant.

Animal Products

Livestock and animal products, such as meat, dairy products, eggs, hides and furs, are of major importance in both agriculture and industry, as well as domestically. Their chemurgic significance is so well understood generally that it is not dwelt upon in detail here.

The meat packing industry offers a good example of the completeness with which raw materials are utilized. Aside from the various edible portions of an animal the inedible remains are almost completely utilized. The hides, skins, wool, and hair find numerous familiar uses. The fats and greases are used in feeds, soap, lubricants, foods, etc., while the glands and other organs yield valuable hormones and enzymes for use in medicines. Blood and bones are made into fertilizers and feeds and the intestines are used to make sausage casings, music strings, tennis strings, and surgical ligatures. Gelatin is derived from hide, connective tissue, and bone cartilage; and glue is made from hide trimmings, sinews, horn piths, pizzles, lips, ear tubes, mammary glands, heads, knuckles, feet, and bones. The precursor of glue is collagen, which forms glue when boiled. Meat scrap tankage finds its way into mixed feeds. Tankage containing horns, hoofs, stomach contents, and guts is used as fertilizer. Even the tank water is evaporated, under reduced pressure, and the resulting sticky mass is incorporated with tankage.

In reviewing the subject of chemurgy it is easy for one to become overoptimistic about the potential use of plant materials in industry. Even though developments of this type require considerable time, through the cooperation of agriculture, science, and industry, remarkable progress has been made and it seems certain that the movement is gathering momentum for a greater future significance.

Nevertheless, it should be kept in mind that the occurrence of some desired material in a plant does not assure its successful development as a workable source. That is only an initial prerequisite. The yield must be satisfactory from the agricultural standpoint, the plant must not present too much difficulty in cultivation and harvesting, the raw material must be readily obtainable and processed with minimum difficulty. And finally, success may be determined by its balance with competitive sources, possible tariff rates, consumer preferences, transportation costs, and many other factors.

A survey of this field leads to the conclusion that many of the chemurgic industries are sustained by agricultural surpluses and wastes. These are fluctuating and uncertain sources of raw material which create an element of insecurity for the dependent industries. ''Agro-industrial'' developments of the future will pay greater attention to the establishment of permanent sources of raw materials. Some industries now find it desirable to contract for the production of their raw materials, and others buy or lease land and supervise directly the raw material production. Through scientific plant breeding crops are being developed to meet the various specifications of the industrial consumer. A more wholesome and permanent integration of agriculture and industry is taking place.

BIBLIOGRAPHY

Bailey, A. E., "Industrial Oil and Fat Products." New York, Interscience Publishers, Inc. (1945).

Bennett, H., "Commercial Waxes." New York, Chemical Publishing Co., Inc. (1944).

Chemurgic Digest, published semi-monthly by the National Farm Chemurgic Council, Columbus, Ohio, 1942 to date.

Clemen, R. A., "By-Products in the Packing Industry." Chicago, Ill., University of Chicago Press (1927).

Furnas, C. C., "Rogers' Industrial Chemistry." 6th ed. Vol. II. New York, D. Van Nostrand Co., Inc. (1942).

Gregory, T. C., "Uses and Applications of Chemicals and Related Materials," Vols. I and II. New York, Reinhold Publishing Corp. (1939 and 1944).

Herrick, H. T., "Agricultural Commodities as Raw Materials for Industry." New York, Chemical Publishing Co., Inc. (in preparation).

Hilditch, T. P., "The Industrial Chemistry of the Fats and Waxes." New York, D. Van Nostrand Co., Inc. (1941).

Hill, A. F., "Economic Botany." New York, McGraw-Hill Book Co., Inc. (1937).

Kerr, R. W., "Chemistry and Industry of Starch." New York, Academic Press, Inc., Publishers (1944).

Schoffelmayer, V., "Here Comes Tomorrow." Evanston, Ill., Row Peterson and Co. (1942).

Sechrist, W. C., and Peck, R. H., *Mo. Agr. Expt. Sta. Bull.* 442 (1942).

Wilson, C. M., "Trees and Test Tubes." New York, Henry Holt and Co. (1943).

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